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Destroying Chemical Wastes in Commercial Scale Incinerators. Facility Report Number 1 - The Marquardt Company

TRW Defense and Space Systems Group, Redondo Beach, Calif

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Incineration tests were conducted at The Marquardt Company, Van Nuys, California, to determine the effectiveness of thermally destroying two selected industrial liquid wastes: ethylene manufacturing waste and hexachlorocylopentadiene (C-5,6). Each waste was burned at three different test conditions to determine the effects of normal operating and equipment variables. Analysis of combustion gas samples indicated destruction efficiencies of over 99.999 percent for each waste constituent. Standard EPA Method 5 tests were performed on stack emissions to determine particulate loading and composition. Analysis of scrubber water samples indicated no increase in organic content compared to fresh scrubber water. Burner head residue formed during incineration of each waste contained no chlorinated organics. Results of these tests indicated that either waste can be effectively destructed in a liquid injection incinerator; however, because of tarry residual, the C-5,6 waste may be better matched to rotary kiln incineration. Estimated cost of destroying an assumed annual production of 15 million kilograms of ethylene waste was $1.8 million capital investment and $1.0 million annual operating costs ($69/metric ton). Cost of incinerating 4.5 million kilograms of C-5,6 per year was estimated to be $1.6 million capital investment and $2.2 million annual operating costs ($488/metric ton).

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This report has been reviewed by the U.S. Environmental Protection Agency and approved for publication. Publication does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of commercial products constitute endorsement or recommendation by the U.S. Government.

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PREFACE

The purpose of this study is to evaluate the environmental, technical, and economic feasibility of disposing of industrial wastes via incineration. This objective is being pursued through a series of test burns conducted at commercial incinerators and with real-world industrial wastes. Approximately eight incineration facilities and seventeen different industrial wastes will be tested under this program. The incineration facilities were selected to represent the various design categories which appear most promising for industrial waste disposal. The wastes were selected on the basis of their suitability for disposal by incineration and their environmental priority.

This report describes the test conducted at the Marquardt Company, which was the first facility of the series. Marquardt manufactures incineration equipment and has a liquid injection test unit which was used for this project. Wastes resulting from the manufacture of ethylene and from hexachlorocyclopentadiene were tested and found to be successfully destroyed by the Marquardt incinerator.

The content of this report is primarily of an objective nature presenting the equipment description, waste analysis, operational procedures, sampling techniques, analytical methods, emission data and cost information. Facility reports similar to this one will be published as soon as possible after the testing has been completed at a facility so that the raw data and basic results will be available to the public quickly.

This report and the other Facility Reports will contain a few subjective conclusions. However, the detailed subjective analysis will be reserved for the Final Report, which will be prepared after all testing is complete.

ACKNOWLEDGEMENTS

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1. SUMMARY

Numerous organic wastes from industrial operations are generated in liquid form. From a physical point of view, they are often suited for disposal in commercial liquid injection incinerators. If a given liquid waste possesses a significant heating value, it may be a candidate for heat recovery by utilizing it as a supplementary fuel or by combustion-for example-in a water wall incinerator. Ideally, such a high heating value waste would have a relatively low toxicity level, little ash content, minimal suspended solids, be pumpable at ambient temperatures, and annually generated in significant volumes. At the other end of the spectrum are those liquid wastes which are quite hazardous and have low heating values. Organochlorine wastes represent an excellent example of this class of waste. Annual waste quantities generated tend to be large, hence the disposal problem is significant. Solids loadings and ashing characteristics will vary. Because of the hazardous nature of these liquid wastes, however, thermal destruction appears to be a desirable disposal method relative to other alternatives.

Two representatives of liquid organic industrial wastes were selected for incineration at The Marquardt Company facility. In great measure, they exemplify extremes of this generic waste form. The two wastes selected for incineration were those resulting from the manufacture of ethylene and hexachlorocyclopentadiene (C-5,6). On the one hand, ethylene manufacturing waste is a relatively nonhazardous, high heating value waste. It is generated at a rate of approximately 15 million kilograms per year

This waste was a clear light brown solution with no apparent sediment or particulate at room temperature. Indeed, it possessed physical and chemical properties not unlike distillate oil. For example, this waste had a specific gravity of about 0.9 and a heating value of around 10,000 kcal/kg. Its chemical composition was approximately 89 percent carbon and 9 percent hydrogen. Halogens-as chlorine-were about 0.004 percent. Sulfur and nitrogen contents were relatively low; namely 1.32 and 0.13 percent, respectively. Ash content (nonvolatile inorganics) in this waste was less than 0.01 percent. A viscosity of 1.28 centistokes (at 22°C) allowed this material to be pumped and injected into the incinerator without preheating or other conditioning. In reality, this waste appears to be a good candidate for use as a supplementary fuel.

Conversely, hexachlorocyclopentadiene manufacturing waste (4.5 million kilograms annually) was significantly different in comparison with the ethylene waste. This highly chlorinated waste would not sustain combustion without auxiliary fuel. Its heating value was only 2,400 kcal/kg. Physically, the C-5,6 waste was a dark brown dense and viscous liquid with suspended, wax-like particulate matter. Specific gravity of the C-5,6 was in excess of 1.7, while its viscosity at room temperature was 11.3 centistokes. Fortunately, this waste was miscible in No. 2 fuel oil which facilitated injection and combustion in a liquid incinerator.

Selection of hexachlorocyclopentadiene waste is important since it represents a class of heavily chlorinated wastes. Safe destruction of this hazardous material is indicative of what may be anticipated by incinerating similar organochlorine wastes. Further, C-5,6 is the princi- intermediate for synthesis of important polychlorocyclodiene pesticides, including chlordane, haptachlor, aldrin, dieldrin, isodrin, endrin, mirex and kepone. In this regard, prolonged storage of such pesticides can result in product degradation in which C-5,6 may be formed. Further, incineration of chlorinated pesticides may result in the formation of C-5,6 as an intermediate reaction product. Therefore, adequate thermal destruction of C-5,6 waste suggests that similar wastes as well as unused C-5,6 based pesticide formulations could be safely incinerated with a significant degree of confidence.

Incineration tests with these two wastes were conducted at The Marquardt Company facility, Van Nuys, California. The purpose of the tests were to determine the effectiveness of thermally destroying these two different wastes from a combustion standpoint; and to insure that incineration could be accomplished in an environmentally safe manner. Marquardt's incineration facility was chosen for a number of reasons. Basically, it is a liquid injection system and thus compatible with the waste form. Further, the incinerator was capable of combustion temperatures in the 800°C to 1400°C (1500°F to 2500°F) temperature range desired for adequate waste destruction. In addition, a caustic venturi scrubber was available to neutralize HCl formation derived from combustion of the heavily chlorinated C-5,6 waste.

Marquardt's liquid injection incinerator consisted of a SUE® (for SUdden Expansion) burner; air, waste, and auxiliary fuel feed systems; and a high energy venturi scrubber. The incinerator was a well-instrumented test unit but similar in operation to their commercial configuration. Marquardt has numerous commercial incinerator installations of this basic system in field operation. The incinerator is scaled up to process larger waste throughputs by simply adding more basic units with proper manifolding, controls and an appropriately sized scrubber. In this regard, the test incinerator was very representative of typical Marquardt commercial installations. Further, the incinerator is setup to use No. 2 fuel oil as an auxiliary fuel; a necessity with low heating value fuels such as C-5,6 waste.

Each waste was burned at three different conditions to ascertain the effects of normal operating and equipment variables as well as attempting to define minimum destruction requirements where feasible. Ethylene waste incineration proved relatively straightforward and trouble free. In reality, its combustion characteristics were quite similar to No. 2 oil, although some solid residue formation was apparent following long duration runs.

The C-5,6 waste presented obvious problems associated with a liquid injection and feed system. Waste suspended solids tended to clog filters rapidly. Smaller particulate passing through a filtration system will, after prolonged operation, abrasively erode injection orifices. This can be minimized by premixing the C-5,6 with fuel oil in holding tanks and allowing the particulate to settle. In any event, a steam or electrically heated and insulated waste feed system would be necessary where premixing, settling or other processing takes place at ambient temperatures less than 20°C.

Elemental chemical analysis of the C-5,6 showed the following composition: 20.76 percent carbon, 0.67 percent hydrogen, 0.37 percent N, 0.02 percent S, and 76.47 percent halogens as chlorine. The chlorinated species were predominantly C_5Cl_6 (hexachlorocyclopentadiene) and C_5Cl_8 (octachlorocyclopentane). As a result, incineration of this waste necessitates use of a caustic wet scrubber to remove the large quantities of the HCl combustion product.

As indicated previously, the test program was conducted using three operating conditions for each waste. The ethylene wastes were burned at three different combustion temperatures to evaluate the impact on destruction efficiency. The combustion of C-5,6 however, required a different approach due to the fact it would not support combustion without the presence of an auxiliary fuel. Because of this, there was concern that chlorinated species (principally C_5Cl_6 or C_5Cl_8) would be emitted to the atmosphere as a result of incomplete destruction at lowered combustion temperatures. For this reason, it was arbitrarily decided that the fuel/air ratio would be held approximately constant at the highest combustion temperature attainable. Thus to evaluate destruction of C-5,6 under different operating conditions, this waste was burned using three blends of fuel oil and waste.

A summary of the test results is presented in Table 1-1, beginning with the range of test conditions for each waste, including combustion temperature, residence time, and waste feed rate. Standard EPA Method 5 tests were performed on the stack emissions to determine particulate loading and the nature of the particulate. Grain loadings of 20-25 mg/mg^3 were obtained for the No. 2 oil and ethylene waste tests. Particulate loadings of 36 to 113 mg/m^3 were obtained for the C-5,6 tests, but 90 percent of the particulate matter from these tests was found to be sodium salts generated by the reaction of the caustic scrubber with HCl and CO_2. The particulate was analyzed for toxic metals and none were found to exist above 0.1 mg/m^3 in the stack gases.

The stack gases were sampled for hydrocarbons and SO_x on all tests, and for HCl, Cl_2, and phosgene on the C-5,6 tests. The only specie detected was SO_x at levels consistent with the fact that the ethylene waste contained more than 1 percent sulfur. The limits of detection for the other species are discussed in Section 4.4.

Benzene and mesityl oxide were found in the test filter and sorbent trap samples at levels which ranged from <0.2 to 2.4 mg/m^3. These levels are about the same as those obtained for the appropriate control samples. Nothing of the less volatile materials, e.g., heavily chlorinated organics, POM, etc., were seen for any of the tests above the lower limits of detection for the analyses. These detection limits were estimated to be 0.1 mg/m^3.

Samples of scrubber water were also analyzed for organic content. Organic material was found in the scrubber water but at the same approximate levels as in the control samples of fresh scrubber water. Gas chromatographic retention data indicates that the same compounds are present in all samples.

TABLE 1-1. Results Summary

	Ethylene Waste	C-5,6 Waste
Combustion Temperature (°C)	1349-1752	1348-1378
Residence Time (sec)	0.14-0.19	0.17-0.18
Feed Rate (kg/min)	1.4-2.0	2.0-2.9(1)
Quality of Stack Emissions:		
Particulate (mg/m^3)	20-25	36-113(2)
Trace Metals (mg/m^3)	0.001-0.003 Pb	0.003-0.006 Pb 0.034-0.065 Mn
Quality of Combustion Gas:		
Total Organics (mg/m^3)	13-22	21-27
Waste Content (mg/m^3)	Not Detected (<0.02)	Not Detected (<0.02)
Trace Metals (mg/m^3)	0.002-0.003 Pb	0.55-1.40 Pb 0.077-0.19 Mn 0.090-0.33 Co
Quality of Scrubber Water:		
Total Organics (mg/l)	Not Significant(3)	Not Significant(3)
Trace Metals (mg/l)	0.02 Pb	0.21-0.54 Pb
Quality of Solid Residue (Clinker):		
Waste Content (mg/g)	1.8-2.4	Not Detected (<.026)
Destruction Efficiency:		
Total Organics (percent)	99.96-99.98	99.97
Waste Constituents (percent)	>99.999	>99.999
Capital Cost ($)	1,818,000	1,630,000
Operating Cost ($/metric ton)	69.31	487.59
Plant Size (Kg/yr)	15 million	4.5 million

(1) Mixture of C-5,6 and No. 2 oil; feed rate of C-5,6 alone is 0.66-1.5 $\frac{kg}{min}$

(2) 85-90 percent of stack particulate content was calculated (based upon sodium analysis) to be NaCl produced by the reaction of the caustic scrubber solution with HCl and CO_2.

(3) Levels not significantly higher than background water samples.

A burner head residue was found to form during incineration of both waste materials. These residues were typically 95 to 99 percent carbon and had some remnants of the fuel feed contained in them at <0.5 percent. Constituents of ethylene waste were easily detectable in the clinker from those runs, but the organics found in the C-5,6 test clinker were not chlorinated.

The waste destruction performance is also summarized in Table 1-1 for both total organics and the specific waste constituents. Emissions and efficiencies are measured at the combustion zone exit prior to the scrubber system. A sample destruction efficiency calculation is presented in Appendix C.

The results of these tests indicate that the C-5,6 waste can be effectively destructed in a liquid injection incinerator. No evidence of C-5,6 or any other chlorinated organic was found in any of the samples including the "coke like" burner head residue referred to as clinker. However, because of the tarry residual in the waste, the C-5,6 may be better matched to rotary kiln incineration, which can accommodate tars and sludges.

Chemical composition, combustion characteristics, and emissions of the ethylene waste are so nearly identical to No. 2 oil that the use of this waste as a primary or secondary boiler fuel should be seriously considered. With the possible exception of the formation of clinker, which appears to have small impact, the incineration of this type of ethylene waste is clean and efficient.

Both capital investment and annual operating costs were estimated for SUE® incineration systems to handle the annual source plant productions of the ethylene and C-5,6 wastes. Annual waste production of the ethylene waste was assumed to be 15 million kilograms (33 million pounds), resulting in an estimated total capital investment of $1,818,000 and annual operating costs of $1,037,500 ($69.31/metric ton). An annual waste production of 4.5 million kilograms (10 million pounds) was used to estimate the C-5,6 waste incineration costs. Total capital investment was estimated to be $1,630,000 with annual operating costs of $2,211,700 ($487.59/metric ton).

2. INTRODUCTION

The objective of this facility test program was to evaluate the effectiveness of thermally destructing specific industrial chemical wastes in an existing commercial scale processing facility. These facility tests are part of an overall U.S. Environmental Protection Agency sponsored program involved with selective testing of seventeen different wastes at eight generic types of thermal destructing facilities. The purpose of this test program is to acquire useful disposal technology as well as economic information. This report describes test operations and results of incinerating two different liquid wastes in a commercially available liquid injection incinerator operated by The Marquardt Company (TMC), Van Nuys, California. TMC is a manufacturer of incinerators, not a waste disposal company, and operates a test facility for evaluation of their incinerator with different wastes.

TMC has been involved in combustion research and production of combustion devices for over 30 years, including ramjets, rocket-ramjet hybrids, and rocket engines. Concurrent with the evolution of this advanced technology, TMC developed a burner for in-house use to generate high pressure, high temperature gases for the testing of supersonic ramjets and materials as well as related aerodynamic testing. The TMC burner is called the SUE® (for SUdden Expansion burner) and was ultimately integrated into a full-scale, commercially available incineration system.

The TMC incinerator was selected for use on this program for several reasons. It utilizes a unique liquid injection configuration which has good air/fuel mixing properties. Development and application of the TMC incinerator system has been ongoing for over 12 years; it is commercially available and currently in use at various industrial facilities. As a result, this incinerator concept has been found to be effective in destroying waste propellants and solvents as well as chlorinated hydrocarbons including herbicides and pesticides. TMC's incinerator is a well-instrumented installation equipped with a high energy venturi scrubber for control of atmospheric emissions.

The two materials tested at TMC, ethylene waste and hexachlorocyclopentadiene (C-5,6) waste, were selected based upon physical compatibility with the incinerator, annual waste generation quantities and the hazardous nature of the wastes. Both wastes are liquid and thus suitable for a liquid injection system. Similarly, both wastes are generated in relatively large quantities. Further, they are representative of even larger classes of similar industrial wastes. The ethylene waste has a high heating value and is therefore ultimately a candidate for heat recovery although the present TMC incinerator did not utilize a water wall combustion chamber. Conversely, the C-5,6 material has a very low heating value (requiring auxiliary fuel to sustain combustion), but is heavily chlorinated and quite hazardous. For these reasons, the two wastes were burned in the TMC facility to demonstrate incineration as a viable alternative to landfill disposal.

Although the TMC incinerator tested on this program had a maximum input feed rate of 3.5 liters/min (55 GPH), it is truly representative of commercial scale applications. This is because applications requiring greater feed rates are achieved simply by using multiples of the existing design. A 12.6 liters/min system, therefore, would only necessitate manifolding four TMC incinerators onto a common foundation. Controls and safety devices would be essentially the same as with a single incinerator. In most applications, exhaust gases would be manifolded to a single adequately sized wet scrubber. For these reasons, data generated at the Marquardt test facility are deemed representative of larger systems. In addition, the single TMC unit was both convenient and economic insofar as the EPA program objective of demonstrating waste destruction efficiency. The fact that TMC's facility was very well instrumented facilitated the conduct of a well controlled and environmentally sound test program.

The following report sections describe in detail the incinerator process equipment (Section 3), and the waste destroyed and test and sampling procedures followed (Section 4). Test results are presented and discussed (Section 5), including effectiveness of destruction of the wastes. An estimate of the capital investment and operating costs of disposing of wastes using this type of incinerator equipment is also included in the report (Section 6).

3. PROCESS DESCRIPTION

3.1 FACILITY PROCESS

The Marquardt liquid incineration test facility process is shown schematically in Figure 3-1. Basic system components, shown in Figures 3-2 through 3-4, include:

- SUdden Expansion (SUE®) incinerator
- Radiation cooled reaction tailpipe
- Air supply system
- Waste fuel system
- Auxiliary fuel system
- Instrumentation
- Emission control system

Following is a description of the incinerator and feed system. Facility instrumentation and emission controls are discussed in subsequent report Sections 3.2 and 3.3, respectively.

3.1.1 Incinerator and Reaction Tailpipe

The configuration of the SUE® incinerator and radiation cooled reaction tailpipe is shown in Figure 3-5. The burner consists of an inlet pipe connected to a large diameter combustion chamber by means of a flat plate. Fuel nozzles protruding through the plate spray the fuel radially into the inlet oxidizer stream. Burning occurs in the recirculation zone formed by the flat plate and the combustion chamber wall. An overall view of the combustion chamber and tailpipe is presented in Figure 3-3.

The combustion chamber wall is constructed of 310 stainless steel and is actively cooled by process air prior to its entry into the combustion zone, thus preheating the air to between 150° to 370°C. The reaction tailpipe, also of 310 stainless steel, is cooled by radiation to the environment and provides a hot walled chamber for completion of the incineration process. The mating flanges of the reaction tailpipe are internally water cooled to prevent warping or leakage and are sealed with high-temperature asbestos fiber material. Ports were provided as shown on Figure 3-5 for instrumentation and gas sampling. This unit operates at velocities of 30 to 45 m/sec, depending on mass flow and temperatures, with resulting "stay time" to the end of the reaction tailpipe (and gas sampling ports) of approximately 0.12 to 0.2 seconds. The incinerator was designed for a continuous feed rate of 190 to 230 liters per hour and a maximum wall temperature of 1650°C, and has successfully destructed chlorinated wastes such as herbicides and pesticides.

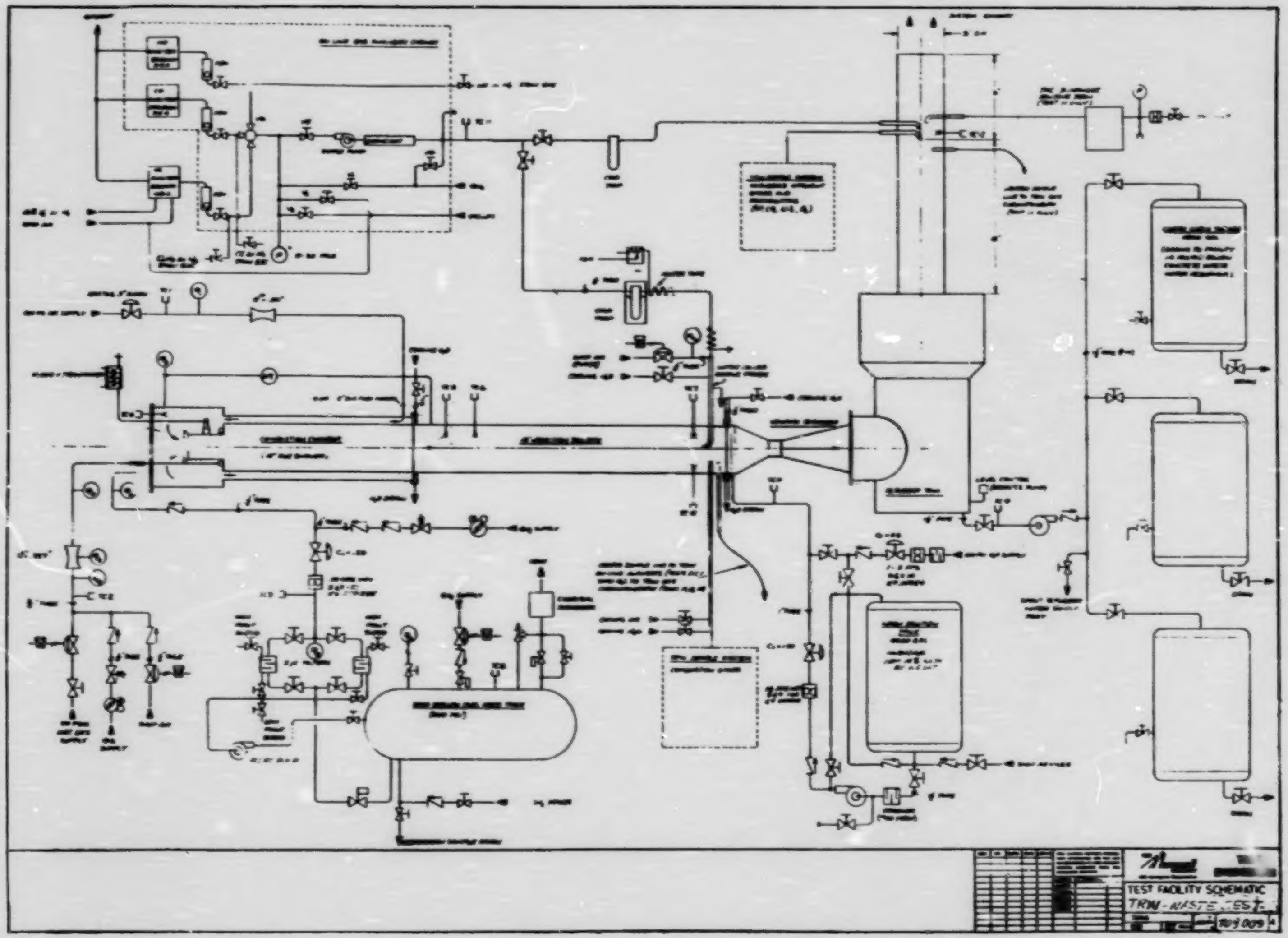
TEST FACILITY SCHEMATIC
TRW-WASTE TEST
309009

Figure 3-1. TMC Test Facility Process Flow Diagram (Figure Courtesy of TMC, Van Nuys, California)

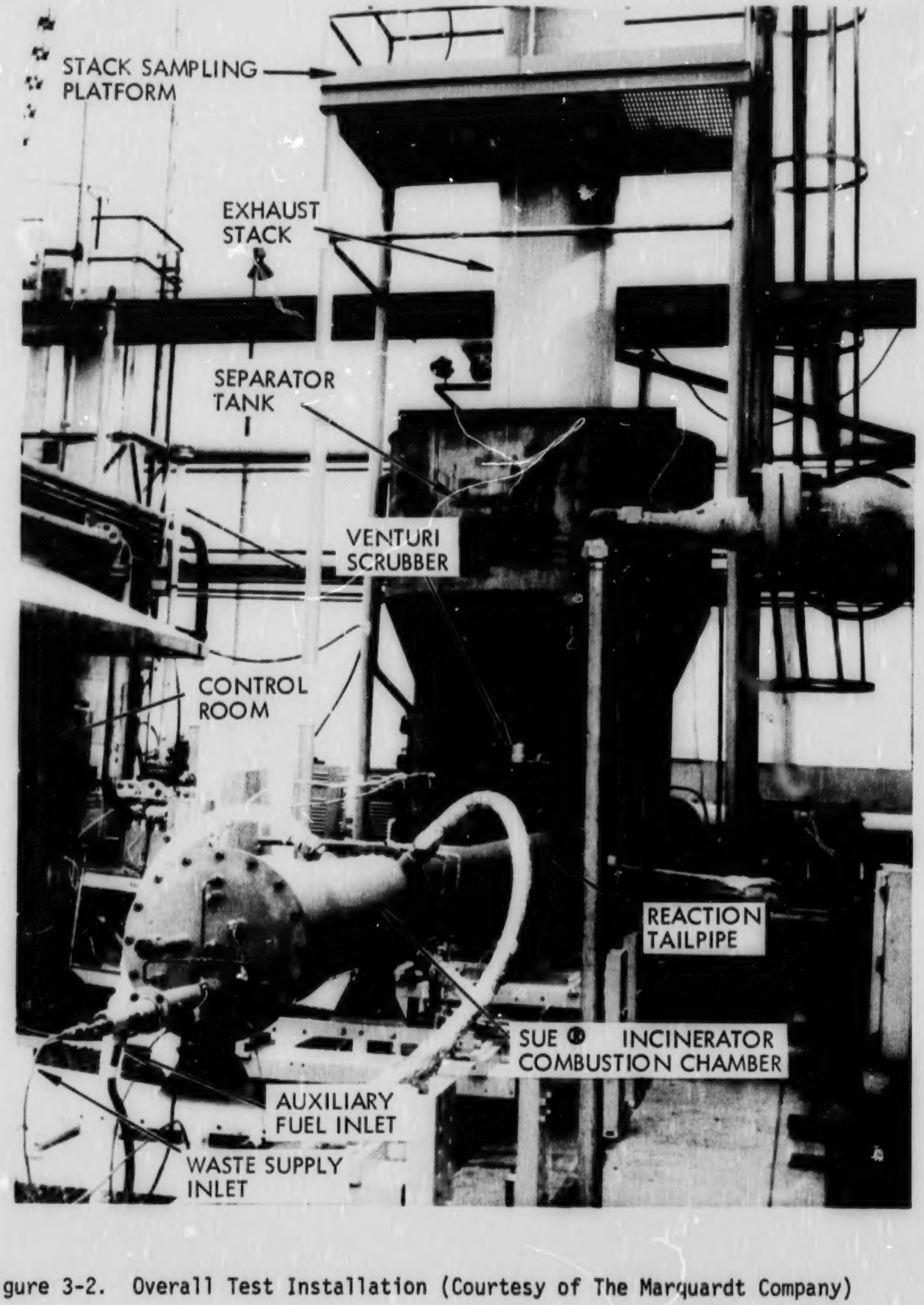
STACK SAMPLING PLATFORM
EXHAUST STACK
SEPARATOR TANK
VENTURI SCRUBBER
CONTROL ROOM
REACTION TAILPIPE
SUE ® INCINERATOR COMBUSTION CHAMBER
AUXILIARY FUEL INLET
WASTE SUPPLY INLET

Figure 3-2. Overall Test Installation (Courtesy of The Marquardt Company)

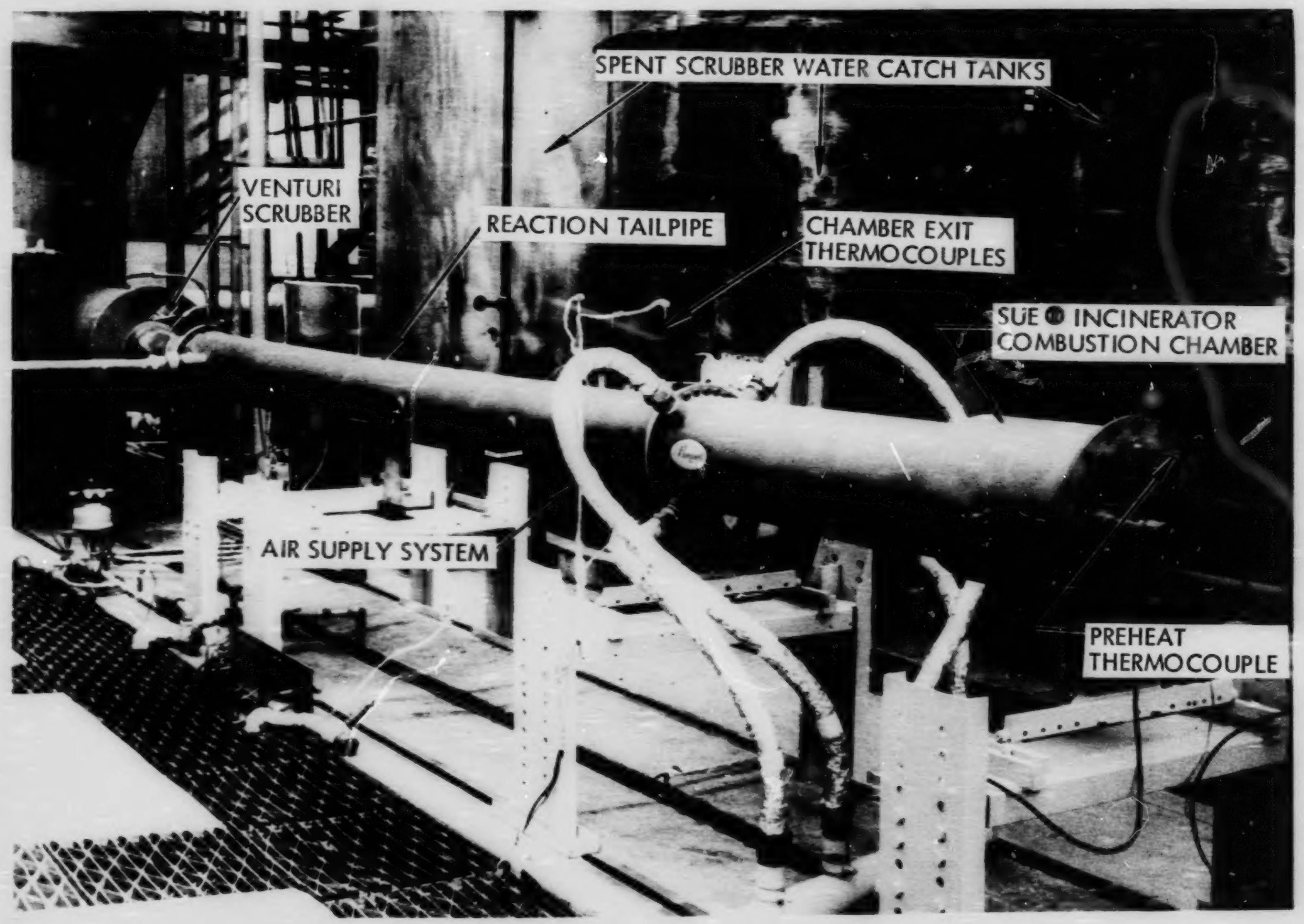
SPENT SCRUBBER WATER CATCH TANKS
VENTURI SCRUBBER
REACTION TAILPIPE
CHAMBER EXIT THERMOCOUPLES
SUE® INCINERATOR COMBUSTION CHAMBER
AIR SUPPLY SYSTEM
PREHEAT THERMOCOUPLE

Figure 3-3. Incineration Unit (Courtesy of The Marquardt Company)

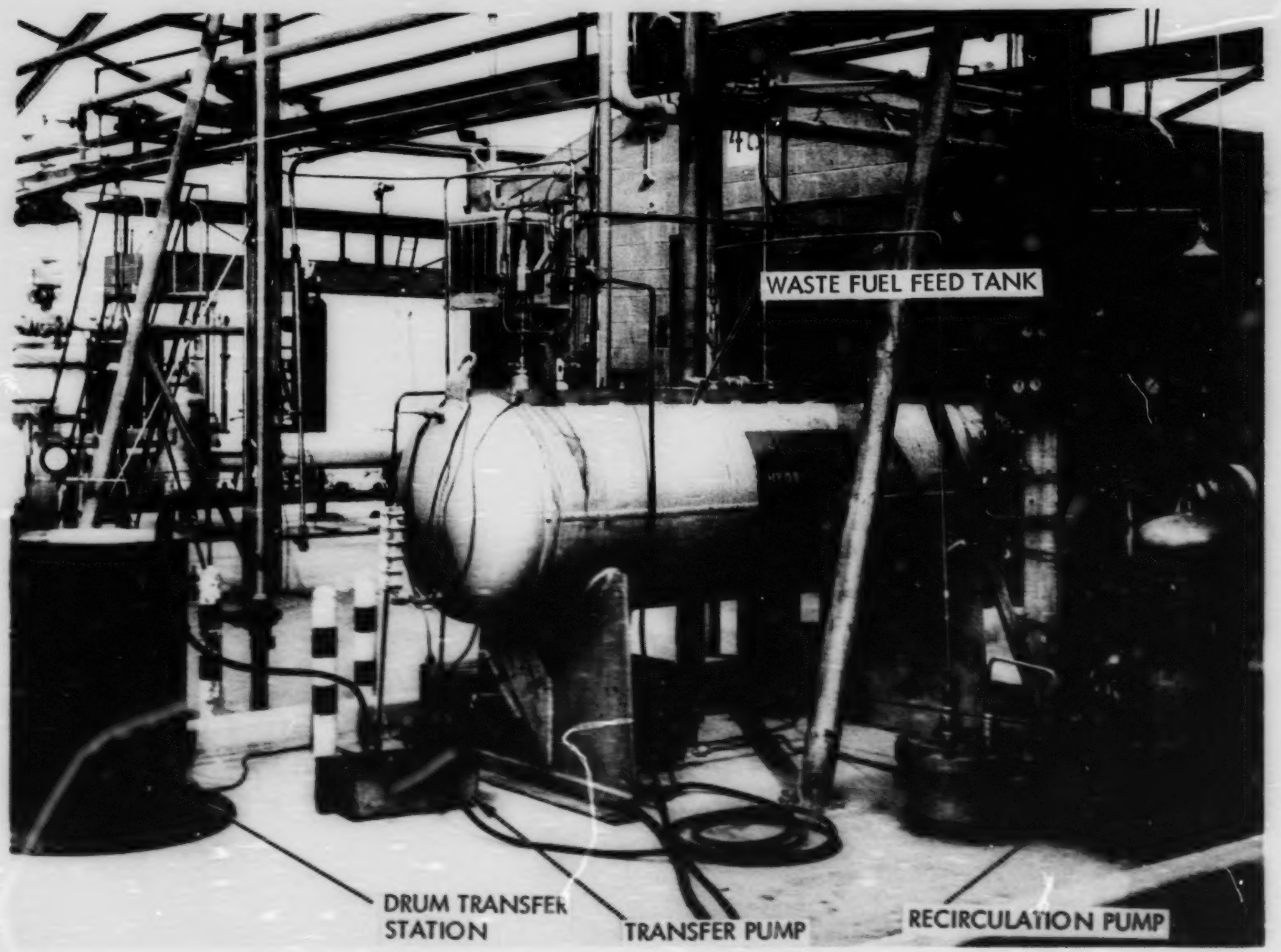
WASTE FUEL FEED TANK
DRUM TRANSFER STATION
TRANSFER PUMP
RECIRCULATION PUMP

Figure 3-4. Waste Fuel Supply System (Courtesy of The Marquardt Company)

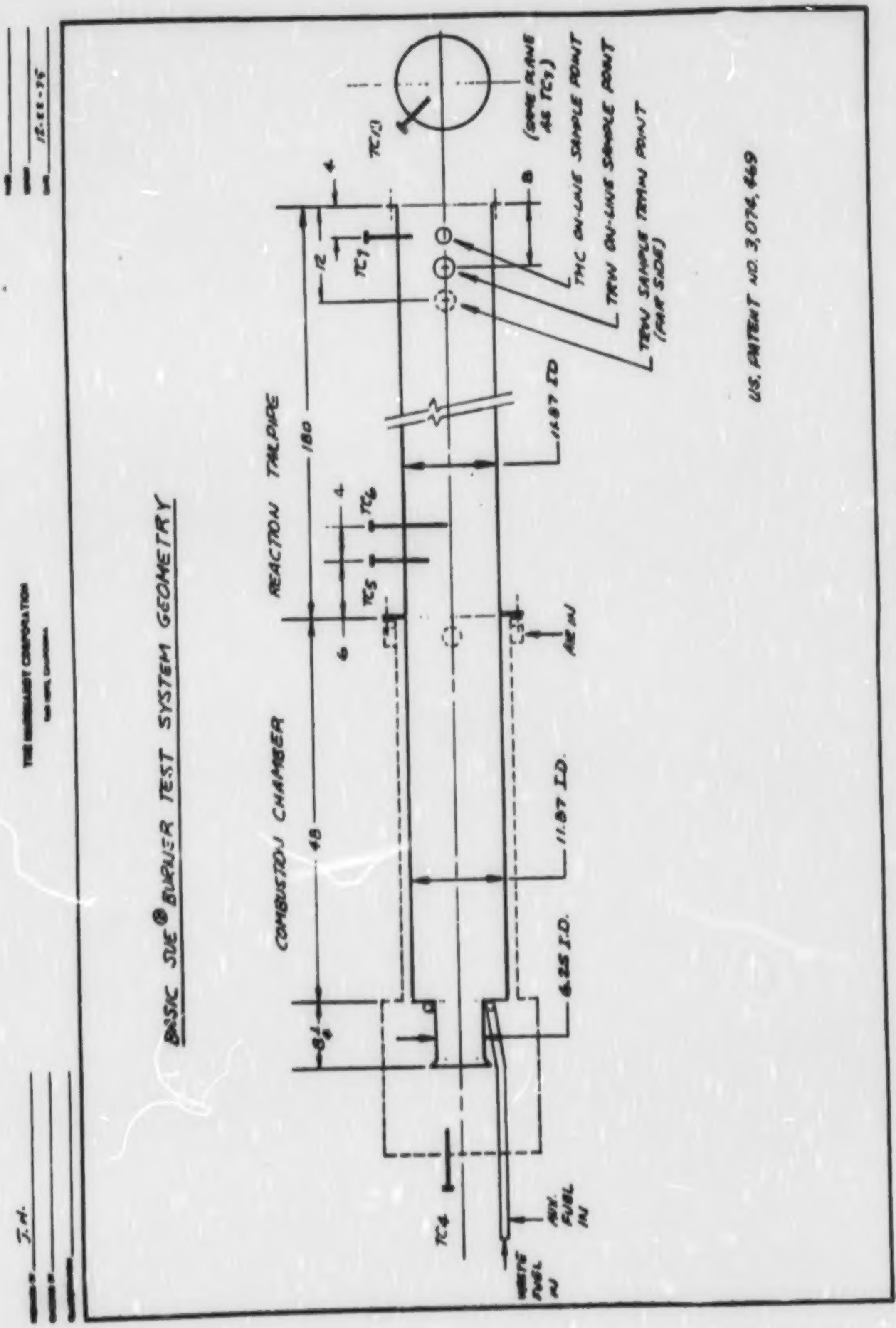
BASIC SUE® BURNER TEST SYSTEM GEOMETRY
COMBUSTION CHAMBER
REACTION TAILPIPE
48
180
6
4
12
4
8
8 1/4
6.25 I.D.
11.87 I.D.
11.87 ID
TC4
TC5
TC6
TC7
TC8
(SAME PLANE AS TC7)
THC ON-LINE SAMPLE POINT
TRW ON-LINE SAMPLE POINT
TRW SAMPLE TRAIN POINT (FAR SIDE)
AIR IN
WASTE FUEL IN
AUX. FUEL IN
US. PATENT NO. 3,074,469
J.H.

Figure 3-5. Basic Burner System Geometry

3.1.2 Air Supply System

Combustion air was supplied from the 4,140-kilopascal (600 psi) facility storage tanks. The Marquardt facility normally maintains a high pressure air supply for ramjet engine testing. Combustion air flow rate is regulated by a remotely controlled valve and metered with a sonic venturi. Air feed lines to the combustion chamber are shown in Figure 3-3. This system is used by TMC due to its availability. Commercial installations utilize conventional forced draft fans for combustion air.

3.1.3 Waste Fuel System

Waste fuel was transferred from 208-liter (55 gallon) drums into a 1,140-liter, 3,450-kilopascel (500 psi) feed tank (Figure 3-4). The tank was pressurized with nitrogen, and fuel was fed to the incinerator through either of two parallel 5 micron filters, a remote control valve, and a turbine flowmeter. The fuel line was purged with N_2 after use. A recirculation system was used to mix the tank contents. In commercial practice, the waste feed would be pumped from a run tank into the incinerator.

3.1.4 Auxiliary Fuel System

The auxiliary fuel inlet to the incinerator is shown in Figure 3-2. Propane gas was used to preheat the incinerator system to an equilibrium temperature of approximately 815°C before introduction of the waste liquid. Once combustion was established with the waste fuel, the propane was turned off and a small air flow introduced into the propane system for burner nozzle cooling. For controlled test purposes, a gaseous nitrogen (GN_2) purge was included to clean the system during shutdowns. All flows were controlled remotely and metered with sonic venturi.

3.2 INSTRUMENTATION

Instrumentation capability provided at the Marquardt facility for this test program is shown on the Figure 3-1 schematic. All instrumentation was calibrated and certified by the Marquardt Standards Laboratory prior to initiation of testing. Measurements were made of all process parameters, including pressures, temperatures, and mass flow rates. In addition, online gas analysis of combustion products was conducted.

3.2.1 Process Parameters

Continuous measurements were made of all pressures, temperatures, and mass flow rates required to control and monitor the incineration process, including the scrubbing and sampling systems. Process instrumentation is listed in Table 3-1. Figure 3-6 shows the process control panel and instrumentation readouts. Direct pressure gauges were located outside of the viewing windows. Temperatures were recorded on 8 or 16 point recorders. Turbine flowmeter readouts were read directly in lbs/sec. Estimated waste flow measurement accuracy was ±2 to 4 percent, depending on whether the flow rate was in the mid range of the calibration or not.

Table 3-1. Instrumentation for Waste Destruction Testing - Marquardt (Refer to Figure 3-1)

System	Symbol	Function	Note	Size or Range
Air	d*	Air flow Venturi	N/A	0.80" dia.
	P_{T_1}	Upstream total pressure	2	0-200 psig
	TC-1	Inlet total temperature	1	0-100°F
Natural Gas or Nozzle Cooling Air/GN_2	d*	Gas flow Venturi	N/A	0.227" dia.
	P_{T_2}	Upstream total pressure	2	0-50 psig
	P_{S_2}	Throat static pressure	2	0-50 psig
	TC-2	Inlet total temperature	1	0-100°F
	P_{T_5}	Manifold pressure	2	0-50 psig
Waste Fuel	W_f	Turbine flowmeter	2	.05-.20 pps
	TC-3	Inlet fuel temperature	1	0-200°F
	P_{T_3}	Manifold pressure	2	0-500 psig
	P_{T_9}	Supply tank pressure	2	0-500 psig
	P_{T_8}	Supply pressure downstream filters	2	0-500 psig
	L_1	Fuel tank liquid level	3	Sight Gauge
	TC-8	Fuel tank temperature	2	0-200°F
SUE Burner	P_{T_3}	Burner inlet pressure	2	0-10 psig
	ΔP_1	Burner pressure drop	2	0-25" H_2O
	TC-4	Burner air inlet temperature	1	0-1000°F
	TC-5,6,7	Exhaust gas temperature	1,2	0-2400°F
Scrubber Systems	W_c	Caustic Solution	2	0.5-1.6 pps
	W_w	Water flowmeter	2	0.5 - 3 pps
	TC-12	Scrubbed effluent gas temperature	2	0-200°F
	TC-10	Scrubber water exit temperature	1	0-200°F
	TC-9	Caustic solution inlet temperature	1	0-100°F
Sampling Systems	P_{T_6}	Beckman probe cooling air	2	0-100 psig
	P_{T_7}	TRW probe purge air	2	0-100 psig
	TC-11	Beckman sample gas temperature	2	0-300°F

NOTES

1. Continuously measured and recorded parameters.
2. Continuously measured but manually read/recorded every 30 minutes or whenever deemed necessary by operational changes.
3. Manually measured/checked and recorded whenever deemed necessary.

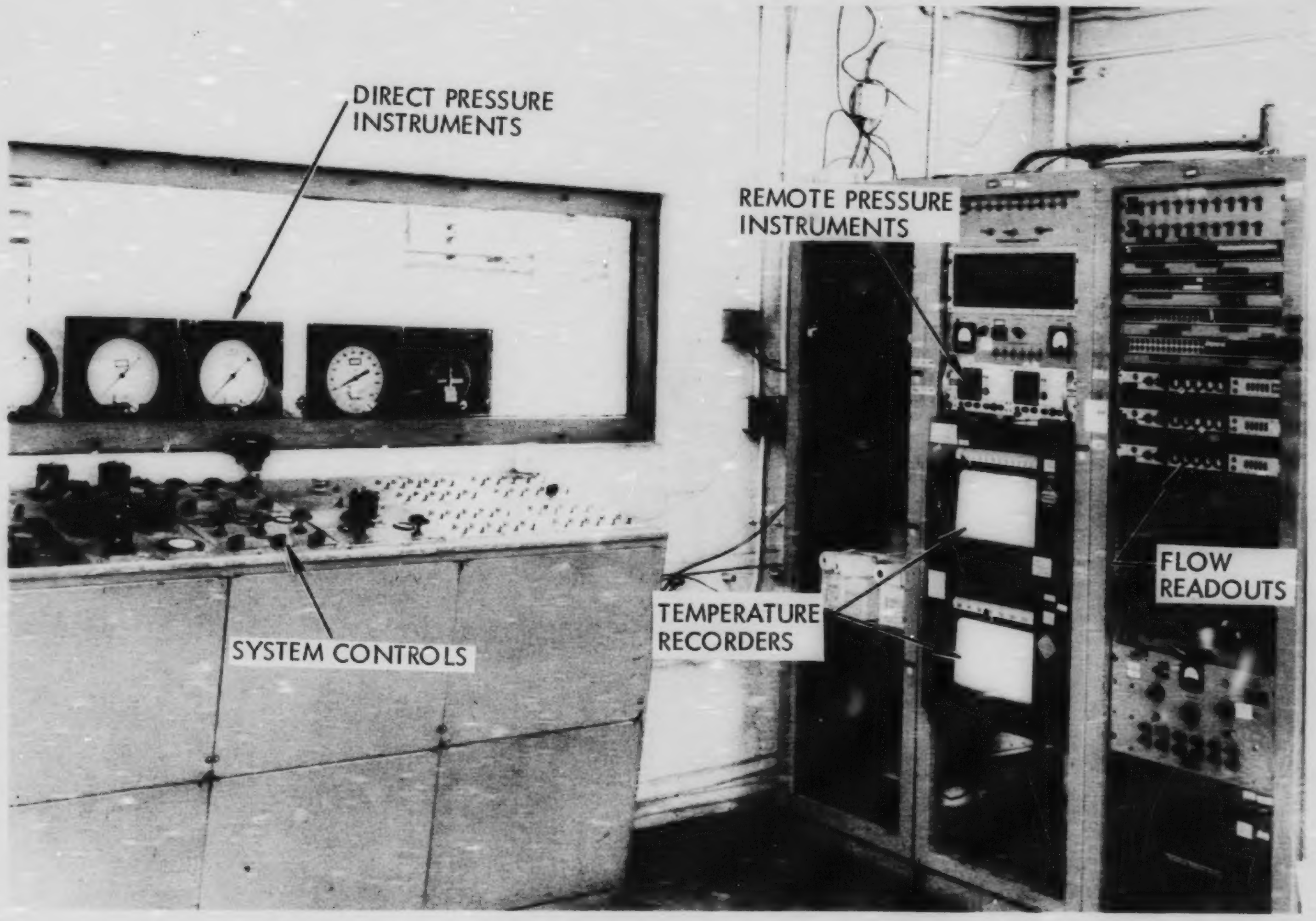
DIRECT PRESSURE INSTRUMENTS
REMOTE PRESSURE INSTRUMENTS
FLOW READOUTS
TEMPERATURE RECORDERS
SYSTEM CONTROLS

Figure 3-6. Process Controls and Instrumentation (Courtesy of The Marquardt Company)

3.2.2 Gas Analysis

On-line continuous monitoring of combustion gas products was performed for all tests using the following instruments (shown in Figure 3-7).

CO - Beckman 315A (Infrared), Span 0-5000 ppm

NO - Beckman 315A (Infrared), Span 0-200 ppm

CH_x - Beckman 109A (Flame Ionization), Span 0-30,000 ppm (Variable)

Valves were provided to allow sampling from either the combustion zone or the stack exit, as shown in Figure 3-1. Data from the combustion zone gas analysis was used to indicate relative system combustion efficiency and to verify attainment of steady state operating conditions prior to initiating gas sampling runs.

3.3 EMISSION CONTROLS

Atmospheric emissions from the combustion of liquid wastes during the Marquardt incineration tests were controlled by a high energy venturi scrubber system. The major components of the scrubber system, shown in Figures 3-2 and 3-3, are described in the following paragraphs. Disposal of spent scrubber liquids is also discussed.

3.3.1 Venturi Scrubber and Separator Tank

Combustion gases leaving the reaction tailpipe passed through the high energy venturi scrubber into the separator tank (Figure 3-2). Quenching and scrubbing water with caustic solution (10-12% NaOH/water) were injected at the venturi inlet and mixed with the combustion gas at velocities up to 125 m/sec in the venturi throat. The separator tank is equipped with a metex screen demistor. Spent scrubber water was collected in the separator tank and transferred to holding tanks (Figure 3-3) by a cyclic pumping system. The water saturated, scrubbed effluent gases were discharged up the stack.

3.3.2 Caustic Solution and Water Supply System

Fresh water to the venturi scrubber was supplied from the 965-kilopascal (140 psi) facility water system at the rate required to quench the gases and scrub at a rate of approximately 19 liters/min per 28 actual cubic meters per minute. When burning the C-5,6 waste, caustic solution was also injected to neutralize the HCl and Cl_2 in the combustion products . Caustic flow (approximately 12 percent NaOH in water) was injected at a rate about three times the amount required to neutralize the theoretically expected amounts of HCl. Both flows were regulated by remote control valves and metered by turbine flowmeters.

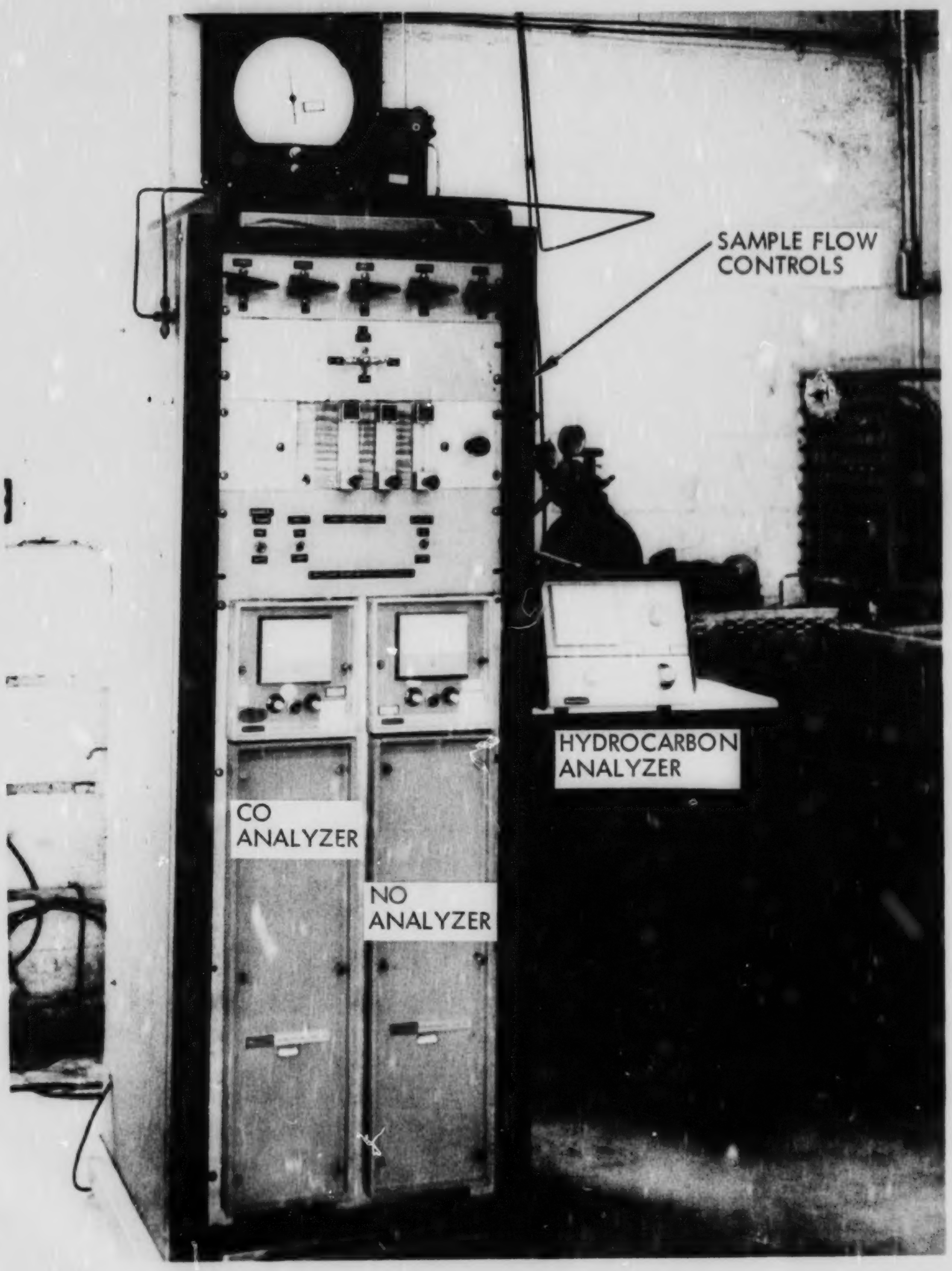
SAMPLE FLOW CONTROLS
HYDROCARBON ANALYZER
CO ANALYZER
NO ANALYZER

Figure 3-7. TMC On-Line Gas Analysis Equipment (Courtsey of The Marquardt Company)

3.3.3 Scrubber Liquid Collection System

Spent scrubber water was collected in any of three 21-kiloliter (5,500-gallon) catch tanks (Figure 3-3). The pump cycle was monitored to allow taking of samples during actual separator tank pumpout. The collected liquid was discharged to the facility's 5.3 megaliter reservoir. Reservoir water is analyzed and neutralized, if required, before release to the municipal sewer system.

4. TEST DESCRIPTION

This section presents the manner in which the tests were carried out. It is divided into the following subsections, listed in order of discussion:

- Physical and chemical description of the wastes that were tested
- Operational procedures used and a test-by-test commentary
- Sampling methods
- Analysis techniques
- Description of the problems encountered related to the facility and sampling.

4.1 WASTES TESTED

The two wastes selected for testing at TMC were from the manufacture of ethylene and hexachlorocyclopentadiene (C-5,6). Survey samples were received as early as possible before the tests and representative samples were obtained by compositing another sample at the time the waste material to be burned was drummed. These samples were then analyzed for both organic and inorganic composition to determine the expected compounds of interest in the test burn samples.

4.1.1 Ethylene Manufacturing Waste

The ethylene waste was a clear light brown solution with no apparent sediment or particulate at room temperature. It had a strong pungent odor but did not fume when exposed to the atmosphere. The loss on ignition at 800°C (LOI) for this material was greater than 99.99 percent, indicating a very low concentration of non-volatile inorganics. Other physical characteristics of the waste sample were:

- Heat content of 10,050 kcal/Kg (18,100 Btu/lb)
- Specific gravity of 0.91
- Kinematic viscosity of 1.28 centistokes at 22°C

Elemental analyses performed on the ethylene waste showed the composition to be:

carbon - 88.7 percent
hydrogen - 8.6 percent
nitrogen - 0.13 percent
sulfur - 1.3 percent
halogens as chlorine - 40 ppm

4.1.1.1 Organic Composition

Analytical techniques used to determine the organic composition included infrared spectrophotometry (IR), low resolution mass spectroscopy (LRMS), and combined gas chromatography/mass spectroscopy (GC/MS). The IR spectrum revealed the presence of aromatic and aliphatic hydrocarbon structures. All significant peaks correlated to major constituents found in the GC/MS analysis discussed below. No evidence of -OH, -NH, -COOH, -C=O, or any other peaks indicating the presence of other functional groups were observed. Analysis by LRMS indicated alkyl substituted benzenes, indenes, and napthalenes as the primary species. The spectra indicated a rather complex mixture of species, but no appreciable signal was detected for compounds of molecular weight over 170.

The combined GC/MS analysis of the survey sample found eleven species whose chromatographic response was 0.1 percent or more of the total normalized area. The results, summarized in Table 4-1, showed the waste to consist primarily of unsaturated cyclic and aromatic compounds. No organic sulfur compound could be identified which would relate to the 1.32 percent S found by elemental analysis. Thus, the sulfur is most likely present in an inorganic form. These compositional values are based on equal response of all these hydrocarbons to the flame ionization detector (FID). This assumption is adequate for the purpose of identifying major compounds and/or partial decomposition products in the combustion test samples. The representative sample of the ethylene wastes fed to the incinerator was analyzed by GC under the same conditions used to analyze the survey sample. The chromatograms were compared and the results indicated that the two materials were identical except for small differences in the relative peak areas of a few of the smaller peaks. The relative concentrations of the major constituents of the waste remain essentially the same as shown in Table 4-1.

Table 4-1. Composition of Ethylene Manufacturing Waste Representative Sample

Compound	Approximate Concentration (percent)
Cyclopentadiene	<0.1
1, 3, 5-Hexatriene	<0.1
Methylcyclopentadiene	<0.1
Benzene	30.
Cyclohexadiene	20.
Toluene	20.
Xylene	3.
Styrene	20.
Methyl Styrene	0.8
Indene	5.0
Molecular Weight 131 or 132	<0.1
Methylindene and Divinyl Benzene	1.
Naphthalene	3.
Ethyl Naphthalene	0.2

4.1.1.2 Trace Elements

Trace elemental analysis was performed by spark source mass spectroscopy (SSMS). This analysis showed no metals present at greater than 1 ppm levels. A few potentially toxic metals were found at low ppb levels. These elements and their predicted combustion concentrations from the SSMS data, using Run IV as an example for waste feed rate and other operating conditions, are shown in Table 4-2. Of these elements, only Pb and As are susceptible to loss during the dry ashing sample preparation step for SSMS and may be somewhat low. The mercury determination was performed by a highly quantitative atomic fluorescence technique in order to be sure of an accurate measurement. The extremely low concentrations of these elements in the ethylene waste indicate an expectation of correspondingly low emissions.

Table 4-2. Trace Metals in the Ethylene Representative Waste Sample

Element	Measured Concentration in Waste (ppb)	Predicted Concentration Produced by Combustion (μq/m^3)
Cr	14	1.0
Cu	41	3.0
Mn	2	0.2
Pb	16	1.2
As	8	0.6
Hg	70*	4.9
Ba	1	0.1

*Determined by atomic fluorescence

4.1.2 Hexachlorocyclopentadiene Manufacturing Waste

The C-5,6 waste was a dark brown liquid with darker, suspended, semi-solid, wax-like particulate matter. The material had a slight odor but did not fume when exposed to the atmosphere. The material lost 99.96 percent of its mass upon ignition at 800°C, indicating a low inorganic content. Heat content for the survey sample was determined to be 2,400 Kcal/Kg (4,300 Btu/lb). Its specific gravity was 1.74, and its viscosity at 22°C was 11.34 centistokes.

Elemental analyses performed on the C-5,6 waste showed the composition to be:

carbon - 20.3 percent
hydrogen - 0.57 percent
nitrogen - 0.37 percent
sulfur - 0.016 percent
halogens as chlorine - 76.5 percent

4.1.2.1 Organic Composition

Analytical techniques used to determine the organic composition included IR, LRMS, and GC/MS. The infrared spectrophotometric analysis did not reveal the presence of -CH, -OH, -NH, -C=O, -COOH, or any other functional groups other than those attributable to halogenated organics. Most of the major peaks in the spectrum matched those of hexachlorocyclopentadiene, C_5Cl_6. Other peaks matched that of its eight chlorine analogue, octachlorocyclopentene, C_5Cl_8. Low resolution mass spectrometry confirmed the two major species to be C_5Cl_6 and C_5Cl_8. Heating the waste sample and pumping removed the most volatile compounds of the mixture. The residue yielded a mass spectral pattern of higher molecular weight analogues of C_5Cl_6 including the dimer of pentachlorocyclopentadiene. Analogues with molecular weights as high as 470 were noted.

Combined gas chromatographic-mass spectrometric analysis of the survey sample found five compounds whose chromatographic response was 0.1 percent or more of the total normalized area. The results of this analysis are presented in Table 4-3. As mentioned previously, these values are based on assuming an equal response to all hydrocarbons by the FID.

Table 4-3. Composition of Hexachlorocyclopentadiene Waste Survey Sample

Compound	Approximate Concentration (percent)
C_5Cl_6 hexachlorocyclopentadiene	50.
C_5HCl_7 heptachlorocyclopentene	5.
Chromatogram had doublet peak but mass spectrum shows only octachlorocyclopentene, C_5Cl_8	30. 15.
MW 308, chlorinated organic	0.2
MW 281, chlorinated organic	0.1
MW 376, C_5HCl_9 or C_8Cl_8	<0.1

The representative sample of the C-5,6 waste was analyzed by GC using an OV-225 column and compared to the chromatogram of the survey sample obtained under the same conditions. The chromatograms were very similar including even the minor constituents. There was, however, a change in the relative composition of the major constituents. The areas were computed and normalized under the assumption of equal response to equal weights of the major constituents. The composition of the C-5,6 representative sample is shown in Table 4-4. The remaining minor constituents shown in Table 4-2, did not appear to significantly change relative to each other. However these minor constituents increased in the normalization to account for the drop in the level of C_5HCl_7 and C_5Cl_8 from those measured in the survey sample. These changes do not impact the conduct of the test or the analytical methods for the test samples.

4.1.2.2 Trace Elements

Elemental inorganics were determined by SSMS on the representative sample. The highest ppm concentrations found were for innocuous metals, such as Fe @ 82, Si @ 27, Al @ 38, Na @ 34, and Ca @ 25 ppm. Lower and trace ppb levels were found for numerous other non-hazardous elements. The potentially toxic elements, their concentrations in the waste and their predicted combustion concentrations using Run VI for operating condition data (including the dilution with No. 2 oil) are shown in Table 4-5. Of these elements, all have some tendancy to volatilize as chloride salts due to the conditions (high Cl concentration, dry ashing) of their preparation for SSMS analysis. Thus, all of the predicted combustion values could be low, with the exception of mercury which was determined by a highly quantitative atomic fluorescence technique in order to be sure of an accurate measurement.

4.2 OPERATIONAL PROCEDURES

Detailed operating procedures, including both a test plan and a safety plan, were reviewed and approved prior to arrival of the TRW sampling team on site. Procedures and operating conditions were also recorded during the field tests. Following are brief summaries of both plans, a test-by-test commentary on events that took place in the field, and information on the disposal of waste residues.

Table 4-4. Composition of C-5,6 Waste Representative Sample

Compound	Approximate Concentration (percent)
C_5Cl_6 Hexachlorocyclopentadiene	66
C_5HCl_7 Heptachlorocyclopentene	3
C_5Cl_8 Octachlorocyclopentene	29
Other Minor Constituents	2

Table 4-5. Trace Metals in the C-5,6 Waste

Element	Measured Concentration in Waste (ppb)	Predicted Conc. Produced by Combustion ($\mu g/m^3$)
Cr	12,000	400
Cu	1,900	64
Mn	330	11
Pb	7	0.2
As	1	0.03
Hg	10*	0.3
Ba	36	1.2
Co	42	1.4
Se	3	0.1
V	4	0.1

*Determined by atomic fluorescence

4.2.1 Test Procedures

Tests at TMC were run with two wastes, ethylene manufacturing wastes and C-5,6, as previously described in Section 4.1. The basic procedure for each waste test was:

- Fill waste tank, measure specific gravity
- Verify instrumentation and sampling systems ready
- Ignite on auxiliary fuel (propane) and stabilize temperatures
- Activate on-line analyzer system
- Transfer to waste fuel combustion and observe effluent
- Stabilize system thermally
- Extended burn duration
    - Process data acquisition
    - Combustion gas composition data acquisition
    - Combustion zone and stack gas sampling
    - Scrubber liquid sampling

- Transfer to auxiliary fuel combustion
- Shutdown and secure, inspect for and collect samples of deposits in combustion chamber.

The test series for each waste consisted of three burn periods during which a three hour combustion gas sample was acquired at steady state operating conditions. A three hour sample run with No. 2 oil was also required to obtain background data prior to the C-5,6/No. 2 oil mixture runs.

Target test conditions for the ethylene waste were:

- Air flow rate - 680 g/sec
- Fuel flow rate - 27 to 41 g/sec
- Theoretical combustion temperature - 1430° to 1815°C

Initial test conditions for the C-5,6 wastes were:

- Air flow rate - 680 g/sec
- Fuel flow rate - 39 to 66 g/sec
- Theoretical combustion temperatures - 1430° to 1870°C
- C-5,6/No. 2 oil mixture ratio - 1/1 and 1/2 by weight

4.2.2 Safety Procedures

TMC standard safety procedures for handling and incinerating industrial chemicals were observed during this test program, including the following:

- Only authorized personnel with prior approval were permitted in the test area during operations.
- Chemicals were handled only by personnel wearing suitable protective clothing and trained in handling such materials.
- Safety shower and eyewash was available in immediate area.
- All leaks or spills were to be flushed with JP4 and incinerated in the same manner as test wastes.
- Visual observation of the test system was maintained at all times during operation.
- Safety ropes were used to isolate the test area during actual operation.

- Canister gas masks were available to all personnel
  - Masks were placed in easy access in control room
  - Personnel outside control room carried masks
- Emergency medical treatment was available both onsite and at defined outside medical facilities.

4.2.3 Test Commentary

All recorded data for the test burn incinerator operating conditions were provided by TMC and are summarized in Table 4-6. Each test was numbered consecutively by TMC Run Nos. 1 through 15. TRW Run Nos. I through VII were assigned only to runs during which combustion zone and stack gas samples were acquired. The ratios shown in Column 3 for the C-5,6/No. 2 oil are by weight. Certain of the thermocouples (i.e., TC_5 and TC_6, TC_7 and TC_{13}) are redundant and are meant to provide an average temperature at the same point.

After checkout and background data tests with No. 2 oil were accomplished, three test conditions were evaluated with both ethylene and C-5,6 wastes. Initial test conditions included calculated combustion temperature variations from 1315° to 1760°C. Corresponding measured temperatures at the end of the reaction tailpipe where combustion gas samples were taken were 982° to 1150°C.

4.2.3.1 Checkout and Background Tests

A series of tests were conducted with No. 2 oil as fuel to checkout the incineration and sampling systems. A full duration sampling run was then performed to obtain background emission data burning No. 2 fuel oil only.

> TMC Run No. 1: An initial checkout run with No. 2 oil was made to verify operation of the TRW trailer on-line instrumentation as well as to check out the incinerator and scrubber systems. Sampling trains were operated at the combustion zone and exhaust stack, but no actual acquisition of samples was intended. This run was 70 minutes in duration at a reaction tailpipe temperature of 1132°C. Combustion sample gas temperatures were 105° to 110°C at the filter inlet. All systems operated satisfactorily, and preparations were made for full duration sample tests.
>
> TMC Run No. 2: This test was conducted to measure stack gas velocities after a second stack sampling train monorail system was added. Capability was thus provided to make sampling traverses 90 degrees apart. Stack velocity measurements were utilized to select a probe nozzle diameter for isokinetic sampling.
>
> TMC Run No. 3: A baseline sampling test with No. 2 oil was begun at the same operating conditions as TMC Tests 1 and 2. This test, intended as a 3-hour sample run, was terminated after one hour when

Table 4-6 Incinerator System Parameters Data Summary

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
			Process Flow Rates					Temperatures							Calculated Process Parameters									Beckman	
TMC Test No.	TRW Run No.	Fuel and Waste To Fuel Oil Ratio	Air Avg. Kg/Sec	Fuel Avg. Kg/Sec	Scrub. H_2O Avg. Kg/Sec	Scrub. NAOH Sol. Avg. Kg/Sec	Chamb. Press. PT_3 Kilo-Pascals	Fuel TC_3 Avg. °C	Pre-Heat TC_4 Avg. °C	Chamb. Exit TC_5 Avg. °C	Chamb. Exit TC_6 Avg. °C	Smpl. Point TC_7 Avg. °C	Smpl. Point TC_{13} Avg. °C	Stack Exit TC_{12} Avg. °C	Fuel/ Air Ratio Kg/Kg	TC Theo. °C	TC Avg. °C	Chamb. Vel. m/Sec	Stay Time sec	NAOH Applied Avg. kg/Sec	NAOH/ NAOH Theo. Avg.	Excess Air %	Stoic Fuel/ Air Ratio Kg/Kg	Stack HC $PPMCH_4$	Smpl. Point HC $PPMCH_4$
1	–	No. 2 oil	0.694	0.0324	1.42	–	9.65	23	216	1235	–	1132	–	80	0.0470	–	–	–	–	–	–	–	–	3.5	3.5
2	–	No. 2 oil	0.689	0.0312	1.37	–	9.65	27	216	1249	1254	1121	1088	79	0.0450	–	–	–	–	–	–	–	–	–	–
3	–	No. 2 oil	0.689	0.0315	1.36	–	8.96	19	210	1218	1252	1132	1104	79	0.0450	–	–	–	–	–	–	–	–	–	4
4-1	–	No. 2 oil	0.694	0.0182	1.39	–	9.31	14	99	860	849	860	843	69	0.0262	–	–	–	–	–	–	–	–	18	20
4-2	–		0.694	0.0227	1.39	–	9.31	13	143	1029	1029	971	949	74	0.0327	–	–	–	–	–	–	–	–	7	7
4-3	–		0.694	0.0285	1.41	–	8.96	13	182	1174	–	1089	1060	78	0.0411	–	–	–	–	–	–	–	–	7	9
4-4	–		0.694	0.0317	1.41	–	8.96	13	202	1229	–	1138	1113	80	0.0456	–	–	–	–	–	–	–	–	12	14
5	I	No. 2 oil	0.694	0.0301	1.37	–	10.0	13	202	1198	1184	1119	1073	79	0.0433	1646	1371	44.1	0.131	–	–	56.8	0.0679	8	9
6-1	–	Ethylene	0.694	0.0227	1.36	–	10.34	14	135	893	918	885	857	71	0.0327	1131	1001	32.9	0.176	–	–	130	0.0752	–	–
6-2	–	Waste	0.694	0.0273	1.36	–	8.96	14	182	1054	1049	993	960	75	0.0393	1318	1147	36.9	0.157	–	–	91.3	0.0752	9	–
6-3	–		0.694	0.0349	1.36	–	11.03	14	254	1166	1216	1143	1093	79	0.0503	1602	1360	42.7	0.135	–	–	49.3	0.0752	–	–
6-4	II		0.694	0.0330	1.37	–	9.65	16	246	1137	1169	1114	1048	79	0.0476	1535	1308	41.7	0.139	–	–	58.0	0.0752	1.5	1.5
7	–	Ethylene Waste	0.572	0.0316	1.20	–	8.96	21	321	1241	1256	1151	1046	79	0.0553	1726	1412	36.9	0.157	–	–	35.5	0.0752	2	3
8	III	Ethylene Waste	0.567	0.0229	1.19	–	8.96	26	238	1031	1052	960	968	74	0.0404	1349	1156	30.8	0.188	–	–	86.1	0.0752	2.5	2.5
9	IV	Ethylene Waste	0.558	0.0317	1.23	–	8.96	19	381	1229	1244	–	1144	79	0.0566	1752	1448	36.9	0.157	–	–	32.9	0.0752	2	1.5
10	–	No. 2 oil (Rinse)	0.685	0.0295	1.39	–	11.03	22	199	1168	1168	–	1099	79	0.0430	–	–	–	–	–	–	–	–	–	–
11-1	–	C_5Cl_6/oil	0.572	0.0356	1.13	0.34	12.41	14	257	1166	1181	–	1077	79	0.0622	1393	1235	33.1	0.174	0.040	3.8	54.7	0.0962	4	–
11-2		1:2	0.572	0.0295	1.07	0.34	11.72	14	232	1060	1088	–	933	79	0.0515	1201	1097	29.7	0.195	0.040	4.6	86.8	0.0962	5	–
12	V	C_5Cl_6/oil 1:2	0.567	0.0340	1.13	0.27	11.38	24	271	1185	1183	1117	1102	78	0.0596	1348	1228	32.5	0.178	0.033	3.3	61.4	0.0962	5	–
13	VI	C_5Cl_6/oil 1:1.5	0.572	0.0393	1.07	0.37	11.38	18	256	1219	1184	1108	1121	79	0.0687	1370	1242	33.2	0.174	0.044	3.1	54.3	0.106	2.5	–
14	VII	C_5Cl_6/oil 1:1	0.572	0.0490	0.88	0.57	13.44	14	266	1244	–	1142	1154	81	0.0861	1378	1263	33.6	0.172	0.068	3.2	41.1	0.122	<1.0	–
15	–	JP-7 (Rinse)	0.594	0.0322	1.31	0.33	12.41	10	230	1204	1196	1110	1107	78	0.0540	–	–	–	–	–	–		–	<1.0	–

combustion zone gas temperatures at the filter inlet suddenly rose from the normal 110° to 177°C. This higher temperature would have been detrimental to the filter seals, so the test was terminated. Cooling of the combustion gases by an air stream around the quartz probe liner had been satisfactory in prior tests, but appeared to be marginal in cooling capability. Water as well as air was added to the liner coolant flow (Figure 4-14) for subsequent tests.

TMC Run No. 4: This test was conducted to verify the effectiveness of the modified combustion gas cooling system prior to repeating the sampling run. A temperature excursion from 860° to 1140°C as measured at the reaction tailpipe was made by varying the fuel/air ratio of the incinerator. The water/air combustion gas cooling system enabled filter inlet temperatures of 80° to 95°C to be maintained, allowing a considerable safety margin in assuring temperatures of less than 115°C at the filter inlet. Preparations were again made for a full duration sample run.

TMC Run No. 5, TRW Run I: A background run with No. 2 oil for a full 3 hour combustion zone sample time was completed. Stack sampling was conducted for two hours. Temperature at the reaction tailpipe averaged 1095°C, and calculated theoretical combustion temperature was 1645°C (Table 4-6). Residence time in the reaction tailpipe was 0.131 seconds.

4.2.3.2 Ethylene Waste Tests

After completion of the baseline sample tests, No. 2 oil was drained from the feed tank and ethylene waste was loaded.

TMC Run No. 6, TRW Run II: The first test with ethylene waste was performed. Prior to sampling, a 3 point traverse of reaction tailpipe temperatures was made at nominally 870°, 980°, and 1150°C, with corresponding combustion temperatures of 1130°, 1320°, and 1600°C. A 3-hour sample test was made at 1090°C reaction tailpipe temperature and 1535°C calculated combustion temperature. Residence time was 0.139 seconds. Deposits in the combustion chamber after the test were photographed (Figure 4-1) and clinker samples were taken.

TMC Run No. 7: This run was intended as the second ethylene sample test at an increased reaction tailpipe temperature of 1150°C (combustion temperature of 1725°C), and residence time of 0.157 seconds. After one hour of sampling, filter inlet temperature on the combustion zone sample train suddenly dropped from a normal 88° to 93°C, to 16°C and the quartz probe liner was observed to have moved, probably retracting the probe tip through the seal. The test was discontinued, as combustion gases were not being acquired by the sampling system. The probe liner was safety-wired to prevent axial movement in subsequent tests, thus precluding repetition of this leak.

TMC Run No. 8, TRW Run III: The second ethylene run was successfully completed. Three hours of combustion zone sampling were conducted at a reaction tailpipe temperature of 970°C and a calculated combustion

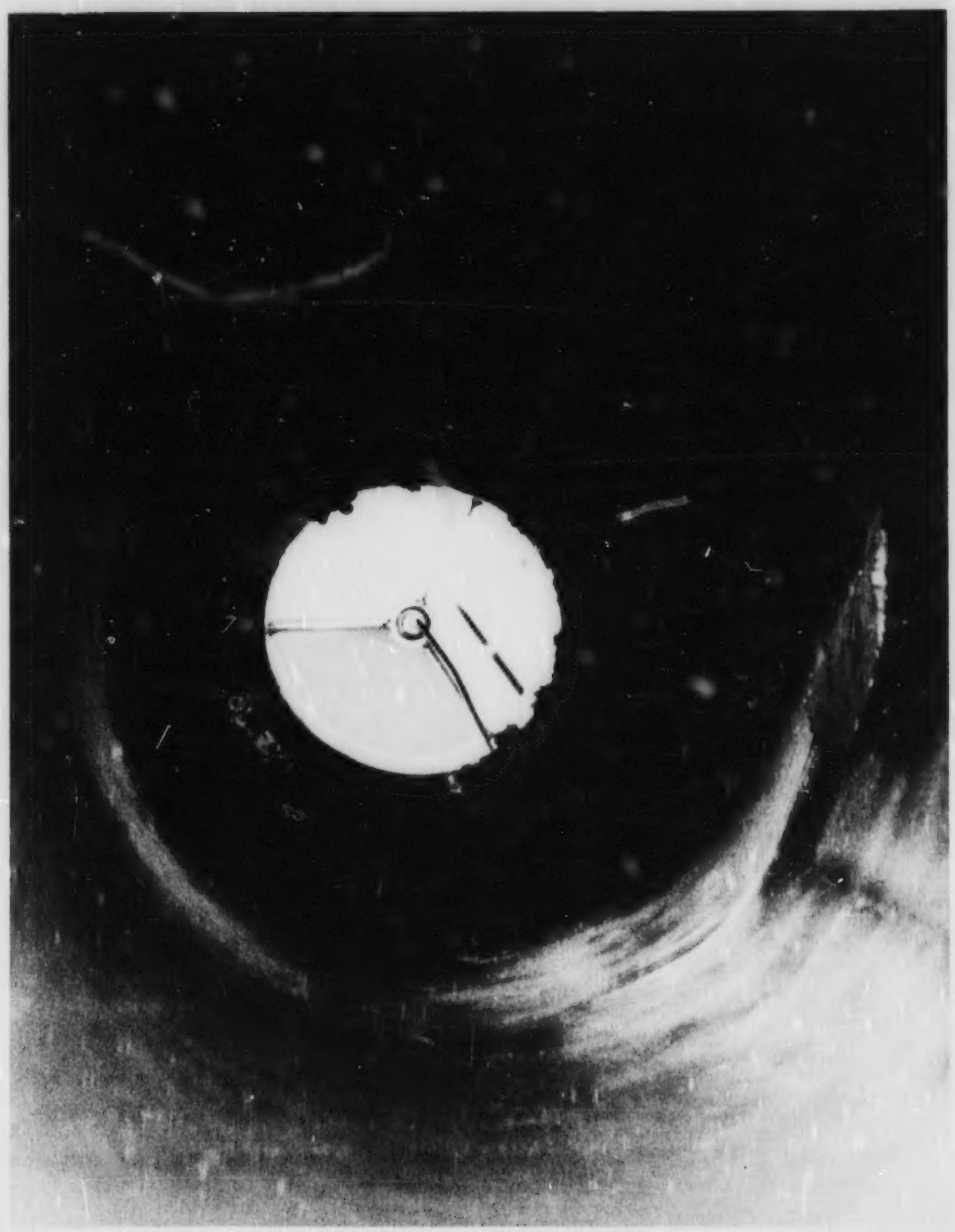

Figure 4-1 MA-II Clinker (Courtesy of the Marquardt Company)

temperature of 1350°C. Residence time was 0.188 seconds. Deposits in the combustion chamber were again photographed (Figure 4-2) and samples taken.

TMC Run No. 9, TRW Run IV: The third ethylene test was conducted at increased operating temperatures. Reaction tailpipe temperature was nominally 1150°C and calculated combustion temperature was 1750°C. Residence time was 0.157 seconds. A 3-hour sample run was completed, although accumulation of deposits in the combustion zone resulted in some excursions in system temperatures during the run. Deposits were photographed (Figure 4-3), sampled, and removed prior to the next run.

TMC Run No. 10: This run was made to flush the system prior to C-5,6 runs by rinsing the fuel tank with No. 2 oil and operating the incinerator on No. 2 oil for over one hour.

4.2.3.3 Hexachlorocyclopentadiene Tests

The heating value of the C-5,6 waste was not sufficient to maintain combustion, and therefore was mixed with No. 2 oil for these tests. Different mixture ratios of C-5,6 to No. 2 oil were incinerated, as noted in Table 4-6 and mentioned in the following test descriptions.

TMC Run No. 11: A checkout run was made with C-5,6 waste. A 15-minute sample was taken with a TMC benzene train for analysis before full duration testing. Laboratory analysis of the sample indicated less than 0.22 ppm of C-5,6 in stack exhaust. A TRW gas chromatograph read hydrocarbon values of 20 ppm, indicative of satisfactory combustion efficiency.

TMC Run No. 12, TRW Run V: The first sample run with C-5,6 was made at a reaction tailpipe temperature of 1107°C and calculated combustion temperature of 1363°C. Residence time was 0.178 seconds. The C-5,6 waste was mixed with No. 2 oil at a weight ratio of 1:2 (1 kg C5,6 to 2 kg No. 2 oil). The test was terminated at 2 hours 15 minutes when caustic solution in the large impinger in the combustion zone sample train appeared to be neutralized by HCl; however, a sufficient sample had been obtained for analyses. Deposits were photographed, (Figure 4-4) sampled, and removed. TMC changed the fuel manifold diameter from 23 to 20 cm to improve combustion in an attempt to reduce deposits. A decision was made to maintain high combustion temperatures of nominally 1370°C, and vary the ratio of C-5,6 to No. 2 oil for subsequent tests.

TMC Run No. 13, TRW Run VI: The second C-5,6 sample run was made at a 2:3 weight ratio of C-5,6 to No. 2 oil. Reaction tailpipe nominal temperature again was 1107°C, and calculated combustion temperature was 1370°C. Residence time was 0.174 seconds. Some fluctuation in system pressures and temperatures occurred due to deposit formations. A full 3-hour sample duration was attained. Deposits were photographed (Figure 4-5) and removed from combustion chamber.

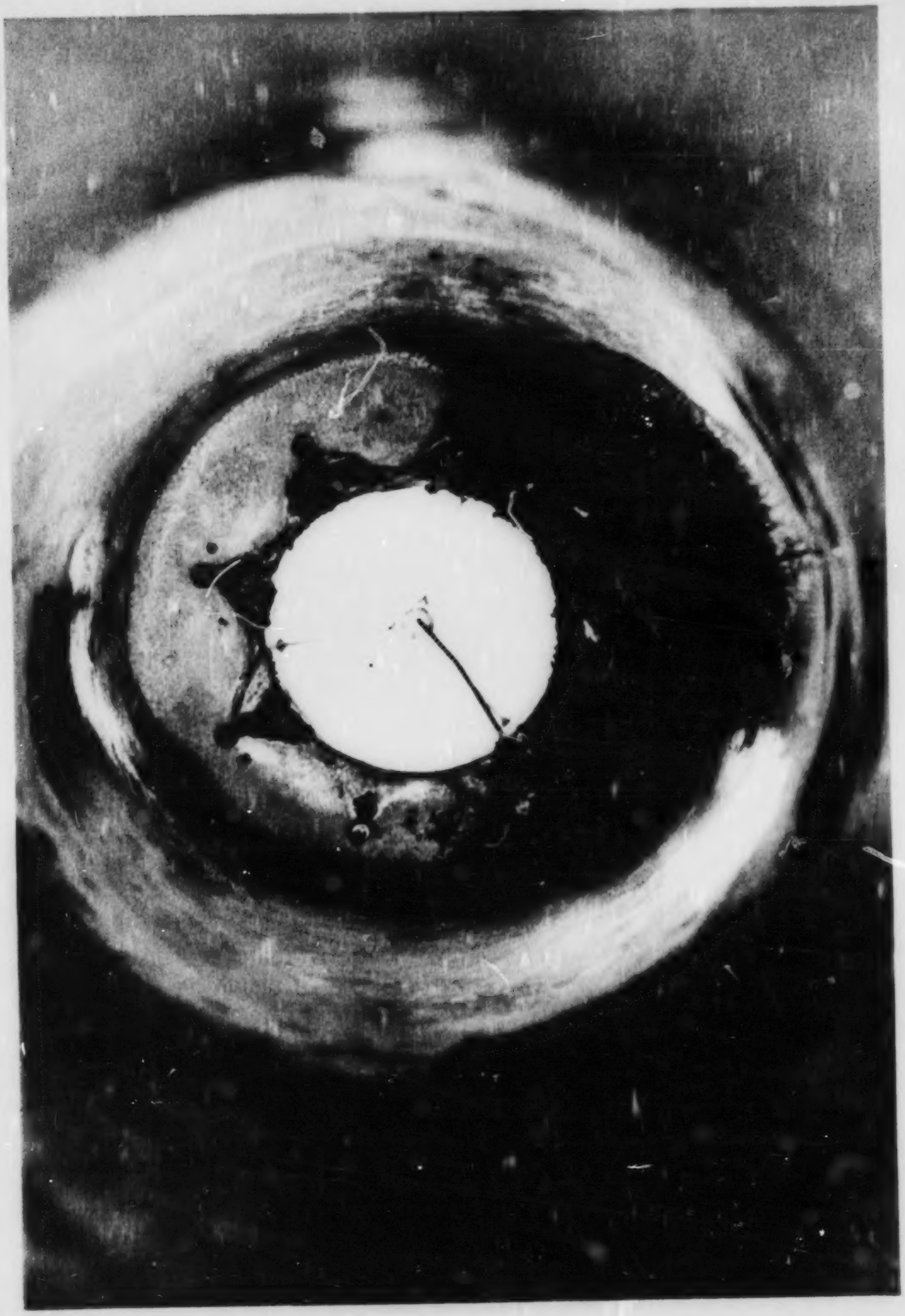

Figure 4-2 MA-III Clinker (Courtesy of the Marquardt Company)

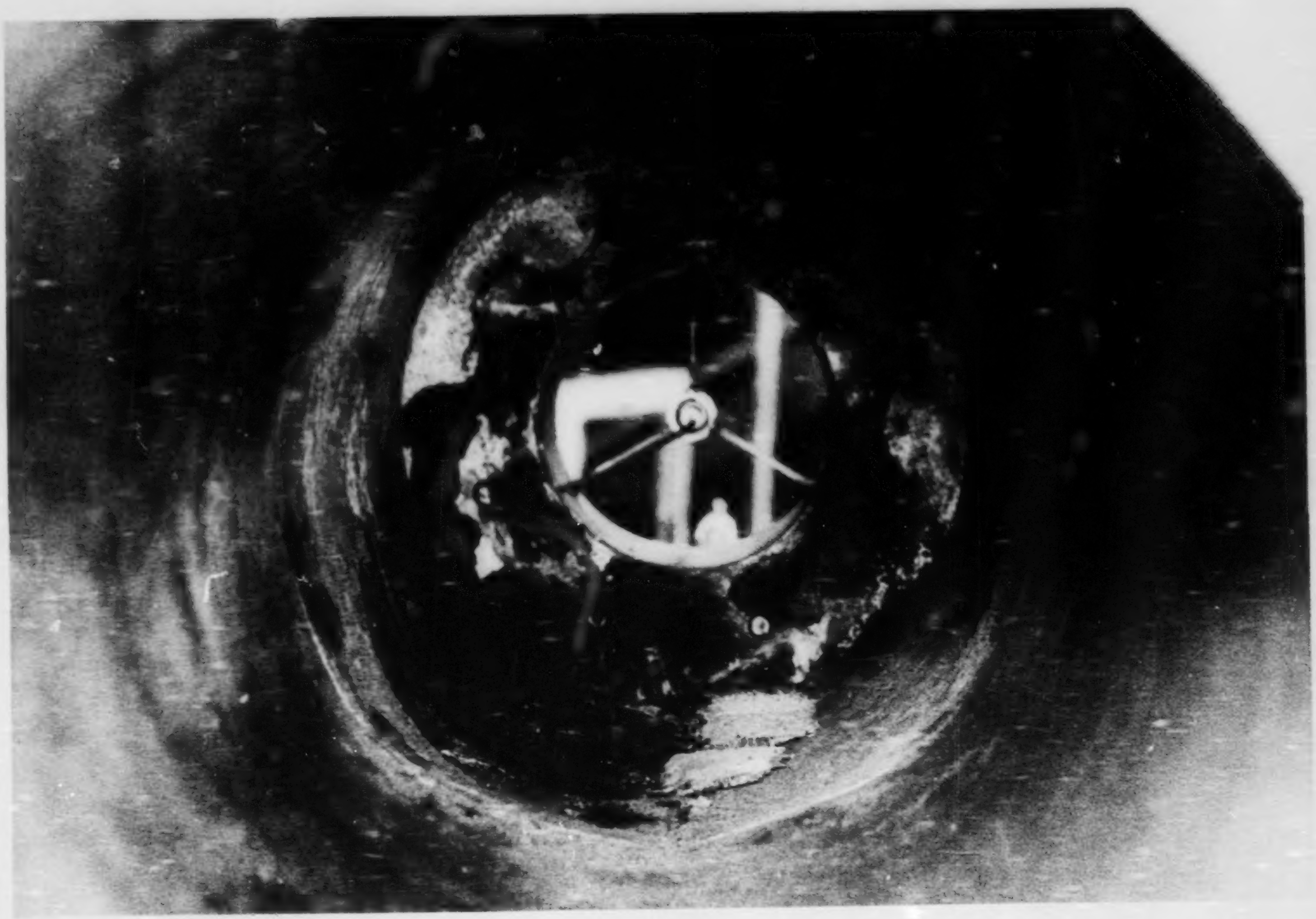

Figure 4-3 MA-IV Clinker (Courtesy of the Marquardt Company)

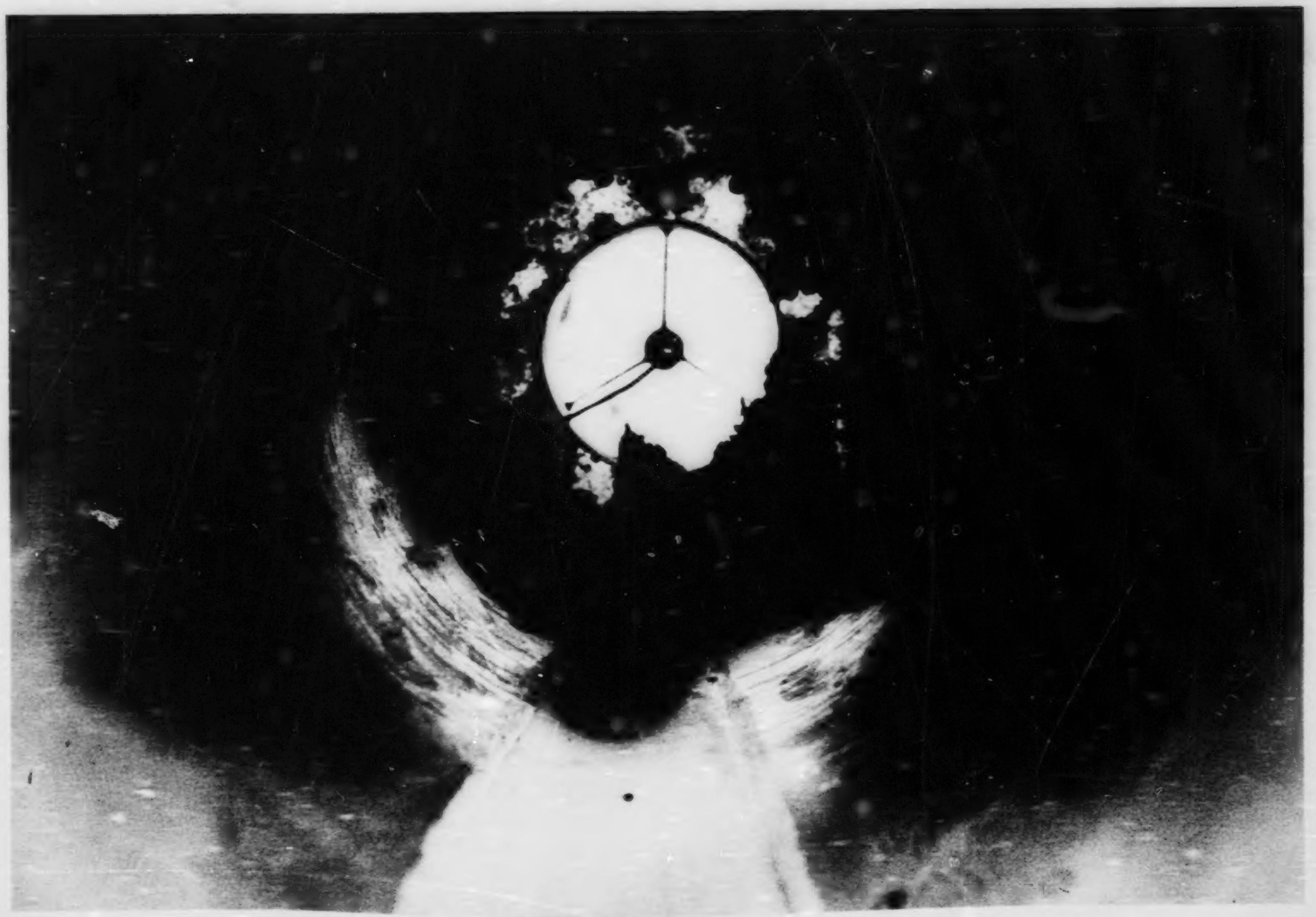

Figure 4-4 MA-V Clinker (Courtesy of the Marquardt Company)

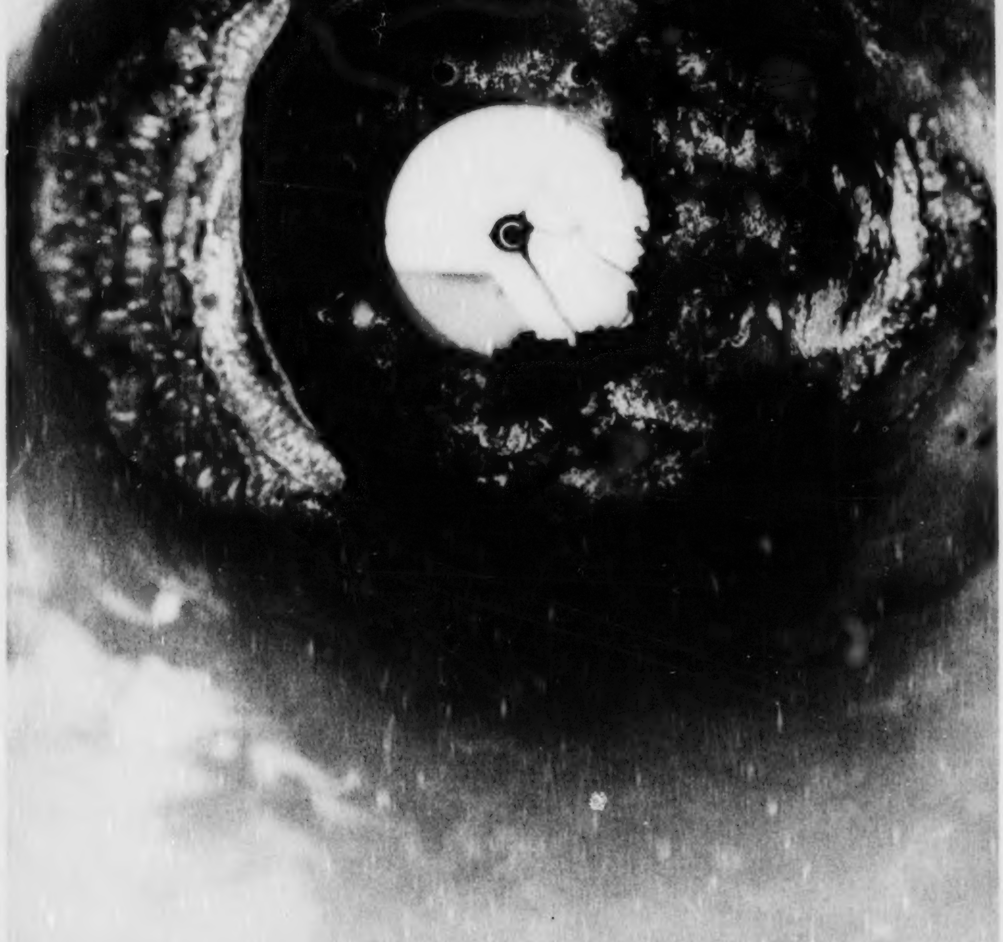

Figure 4-5 MA-VI Clinker (Courtesy of the Marquardt Company)

TMC Run No. 14, TRW Run VII: The third C-5,6 run was made at a 1150°C reaction tailpipe temperature, and a 1378°C calculated combustion temperature. Residence time was 0.172 seconds. Equal weights of C-5,6 and No. 2 oil were mixed for this test. Deposit formations again caused some system fluctuations. Shutdown was premature at about 2-1/2 hours due to depletion of waste fuel in tank. Deposits were photographed (Figure 4-6) and samples taken.

TMC Run No. 15: The fuel tank was rinsed with JP-7, which was then burned for over 1-1/2 hours to flush the system.

4.2.4 Disposal of Waste Residues

The residual ethylene and C-5,6 waste materials along with the empty drums left from the test burns were disposed of by a contract disposal firm in accordance with all applicable regulations.

4.3 SAMPLING METHODS

Sampling methods used in the tests at TMC were chosen to cover three basic areas. These were:

1) Continuous, on-line monitoring of gas composition to determine and follow steady state conditions.

2) Collection and concentration of hot zone combustion products to identify and quantify the trace organic and inorganic species formed.

3) Collection of final emission and waste products to evaluate the environmental safety of the tests.

Following is a brief summary of the methods for each of these areas. More detailed discussions can be found in the Marquardt Analytical Plan.*

4.3.1 On-Line Gas Monitoring

Gases were drawn continuously from the hot zone through a ceramic probe and then through a heated Teflon sample line to the trailer. The location of this probe at the Marquardt test stand is shown in Figure 4-7. The gas then entered the system shown in Figure 4-8. The gas conditioner supplied a cool, dry, particulate free sample to all of the analyzers with the exception of the hydrocarbon (HC) monitor which uses an untreated sample. A heated Teflon line carries the HC gas sample from a tee in the unconditioned sample line to the HC analyzer. Because it uses an untreated gas sample, the HC monitor is the only instrument exposed to the moist acid (HCl coming from the C-5,6 waste burns) stream and is thus the most

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*TRW Document #27033-6001-RU-00, "Analytical Plan for Facility No. 1 Tests to be Conducted at Marquardt Corporation", by J. F. Clausen and C. A. Zee.

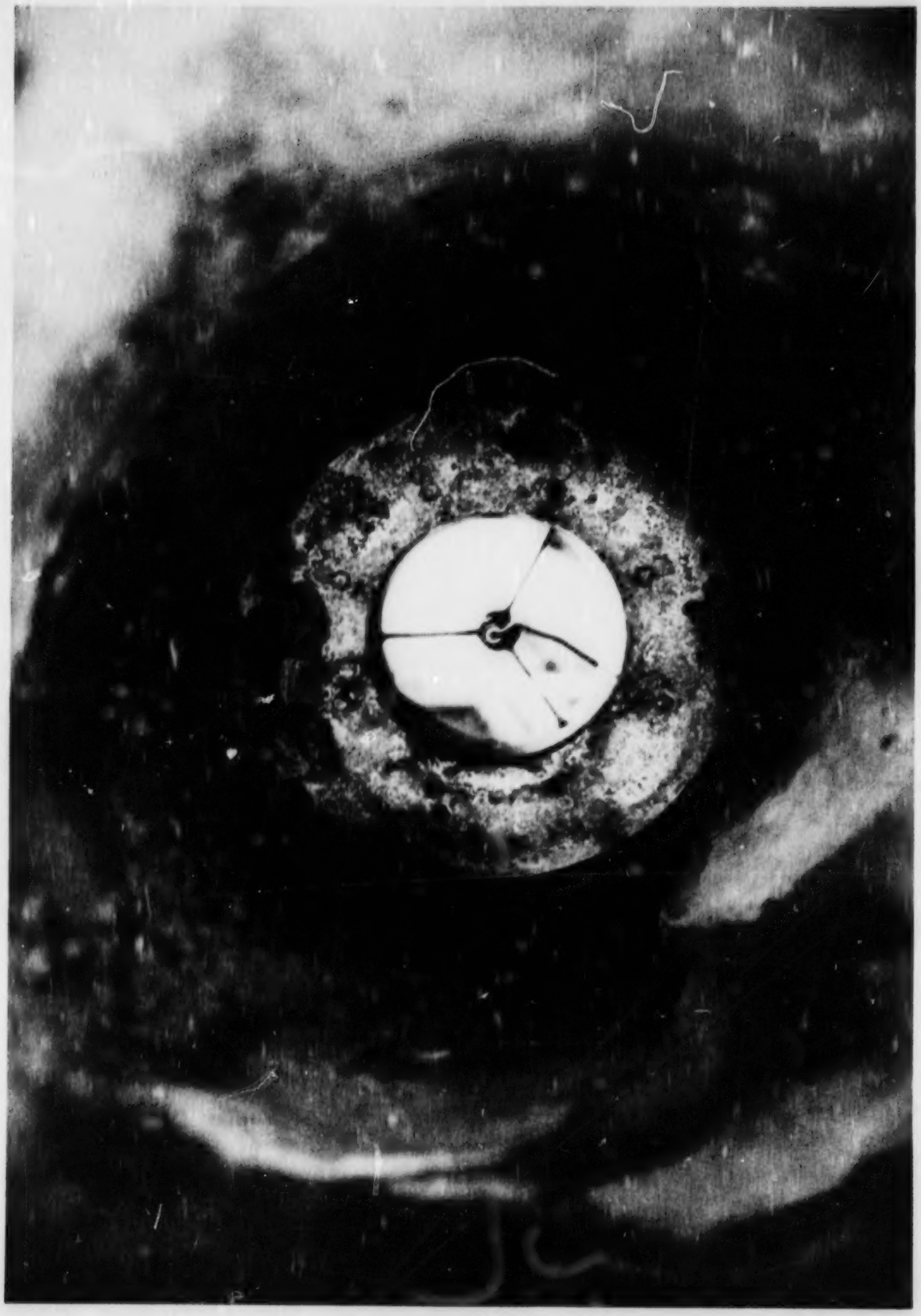

Figure 4-6 MA-VII Clinker (Courtesy of the Marquardt Company)

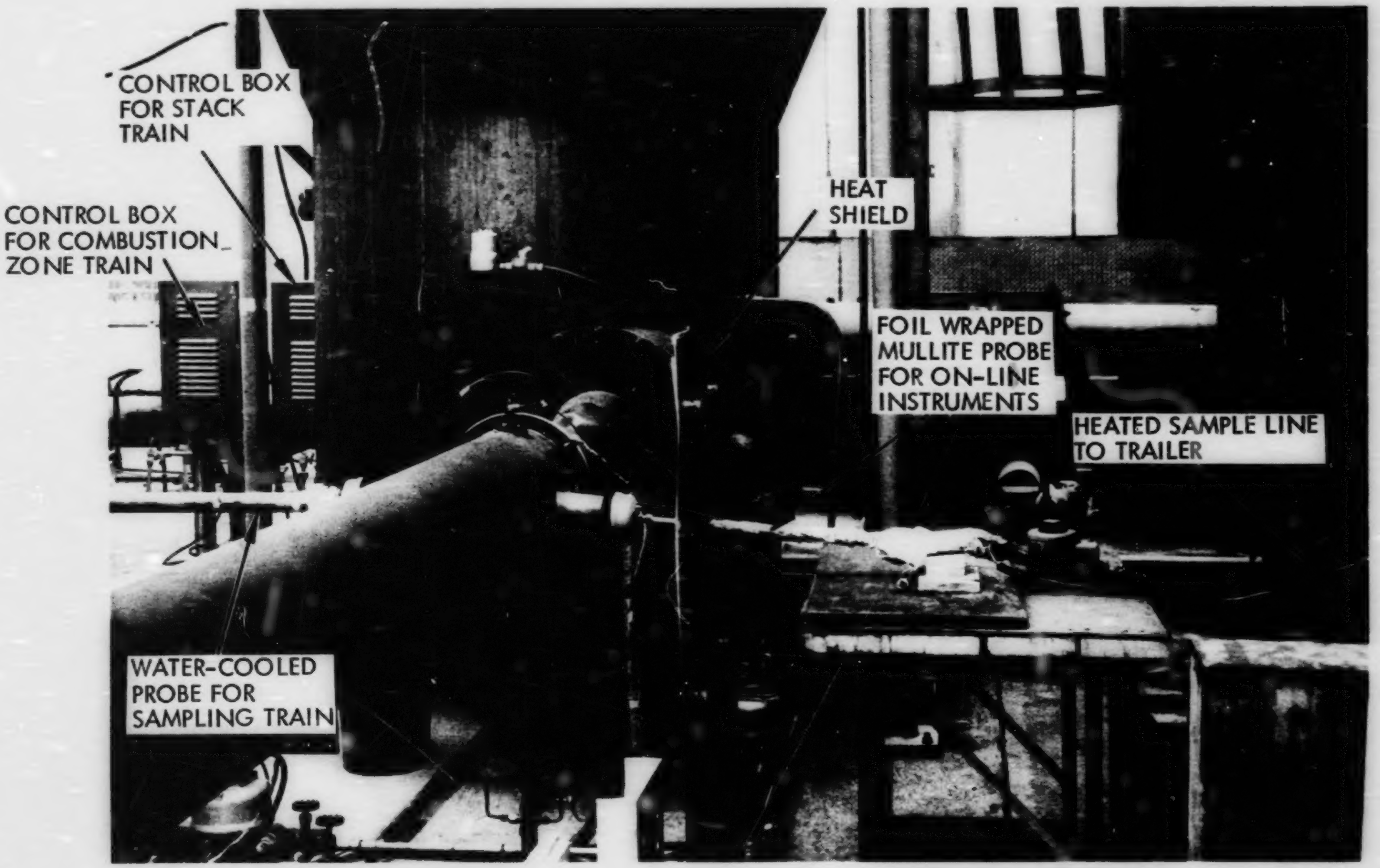
CONTROL BOX FOR STACK TRAIN
CONTROL BOX FOR COMBUSTION ZONE TRAIN
HEAT SHIELD
FOIL WRAPPED MULLITE PROBE FOR ON-LINE INSTRUMENTS
HEATED SAMPLE LINE TO TRAILER
WATER-COOLED PROBE FOR SAMPLING TRAIN

Figure 4-7 Sampling System For On-Line Monitors (Courtesy of the Marquardt Company)

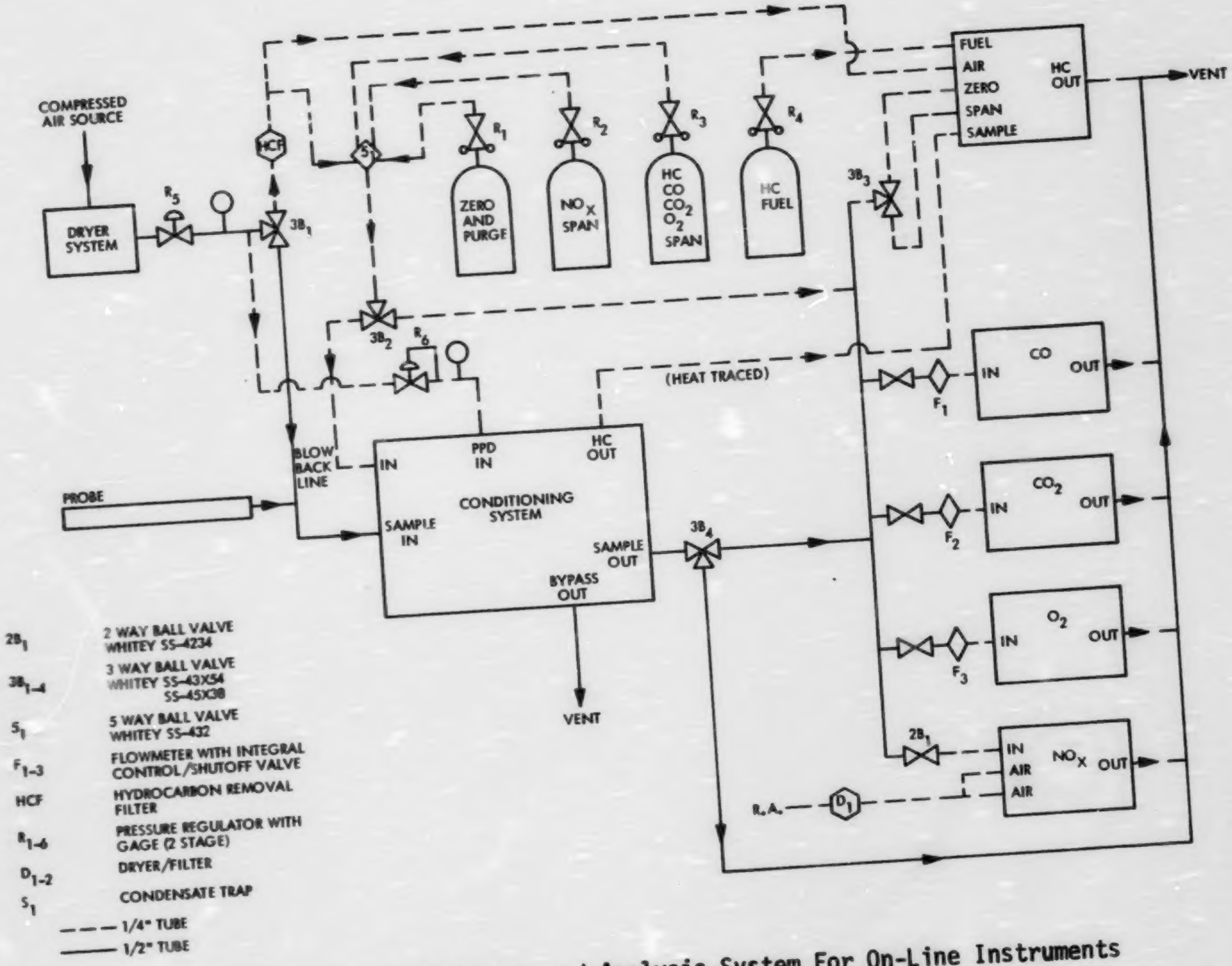
COMPRESSED AIR SOURCE
DRYER SYSTEM
R5
3B1
HCF
S1
R1
R2
R3
R4
ZERO AND PURGE
NOX SPAN
HC CO CO2 O2 SPAN
HC FUEL
3B3
FUEL
AIR
ZERO
SPAN
SAMPLE
HC OUT
VENT
3B2
R6
(HEAT TRACED)
BLOW BACK LINE
PROBE
IN
PPD IN
HC OUT
CONDITIONING SYSTEM
SAMPLE IN
SAMPLE OUT
BYPASS OUT
VENT
3B4
CO
IN
OUT
F1
CO2
F2
O2
F3
2B1
NOX
AIR
R.A.
D1
2B1 2 WAY BALL VALVE WHITEY SS-4234
3B1-4 3 WAY BALL VALVE WHITEY SS-43X54 SS-45X38
S1 5 WAY BALL VALVE WHITEY SS-432
F1-3 FLOWMETER WITH INTEGRAL CONTROL/SHUTOFF VALVE
HCF HYDROCARBON REMOVAL FILTER
R1-6 PRESSURE REGULATOR WITH GAGE (2 STAGE)
D1-2 DRYER/FILTER
S1 CONDENSATE TRAP
1/4" TUBE
1/2" TUBE

Figure 4-8 Gas Conditioning and Analysis System For On-Line Instruments

susceptible to corrosion. To avoid potential problems, a Perkin-Elmer 881 gas chromatograph with an open tubular column and a flame ionization detector was substituted as a total hydrocarbon analyzer during tests with the C-5,6 waste.

The monitoring instruments used are listed with their operating ranges in Table 4-7. Data was recorded on Hewlett-Packard 680M strip chart recorders. Figure 4-9 shows the instrument racks mounted in the sampling trailer. The analyzers, recorders, and manifold valves were all located in racks to provide ease of operation and accessibility. The location of calibration gases and gas conditioning system across from the racks is shown in Figure 4-10, and the work area behind the racks is shown in Figure 4-11.

Table 4-7. Description of On-Line Instruments

Species Analyzed	Manufacturer and Model	Range*
Total hydrocarbons (HC)	Beckman model 402	0.05 ppm – 10% with eight ranges
Carbon monoxide (CO)	Beckman model 865	2-200 ppm 10-100 ppm
Carbon dioxide (CO_2)	Beckman model 864	0.05 – 5% 0.02 – 20%
Oxygen (O_2)	Taylor OA 273	0.05 – 5% 0.25 – 25% 1 – 100%
Oxides of nitrogen (NO_x)	Thermo Electron model 10-A	0.05 – 10,000 ppm with eight ranges

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*All of these manufacturers report an accuracy of ±1 percent of full scale for their instruments.

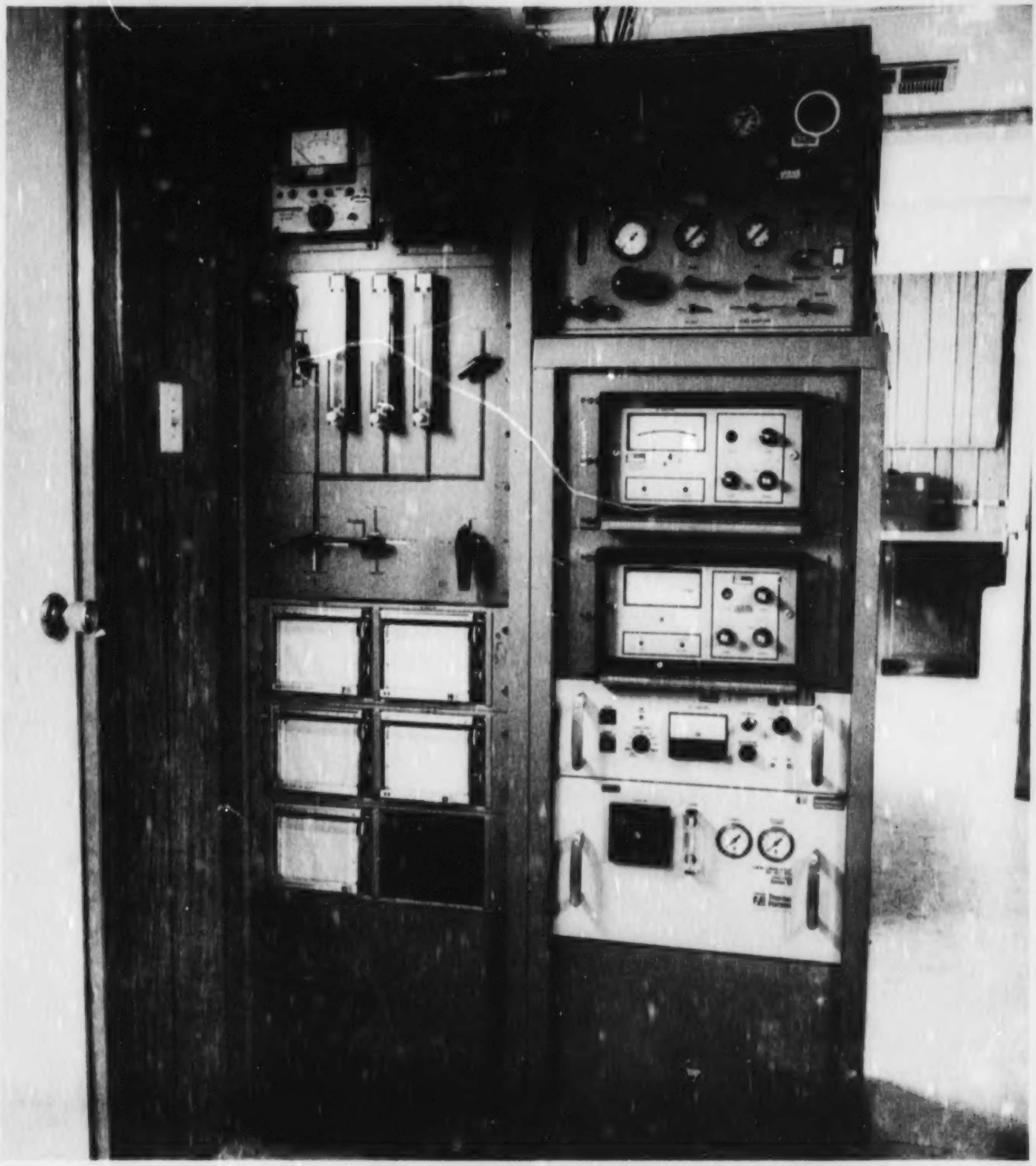

Figure 4-9 Instrument Racks

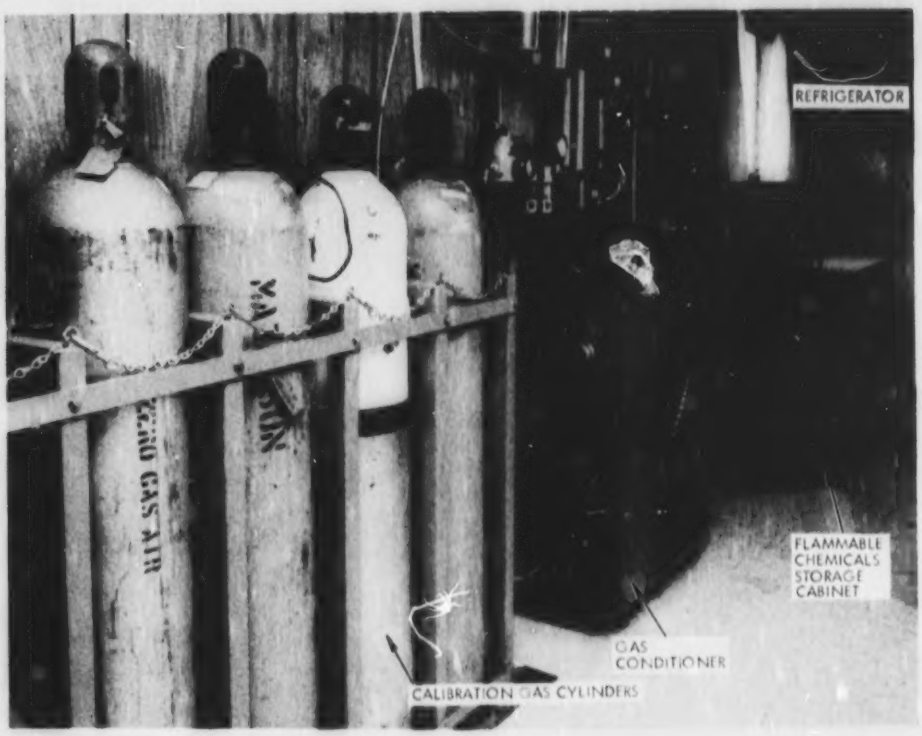
REFRIGERATOR
FLAMMABLE CHEMICALS STORAGE CABINET
GAS CONDITIONER
CALIBRATION GAS CYLINDERS
ZERO GAS AIR

Figure 4-10 Calibration Gases and Gas Conditioner

Figure 4-11 Work Area Behind Instrument Racks

4.3.2 Sampling of Combustion Products

The sampling train used to collect hot zone gases, vapors, and particulate is shown schematically in Figure 4-12 and as set up for a test run in Figure 4-13. It consisted of a standard EPA Method 5 train with the following important modifications.

- There was a stainless steel jacketed, water-cooled probe (shown schematically in Figure 4-14) with a quartz liner. The liner provides an inert surface for the sample gas and the cooled, stainless steel jacket shields this gas from extreme hot zone temperatures in order to quench any further reactions of the sample constitutents. Further cooling of the gas can be modulated by aspirating an air/water mixture into the space between the steel jacket and quartz liner.

- Special fittings were fabricated to allow a back purge of the probe with purified compressed air while the sampling train was not in operation. This eliminated the possibility of contamination from the relatively high amounts of organic, partial combustion products produced during start-up and shut-down of the incinerator. The back purge connection was made at the point where the dogleg from the probe liner mates to the filter.

- A chromel/alumel thermocouple was potted into the dogleg going from the quartz probe liner to the filter housing to check the temperature of the gas stream at that point.

- An ultra high-purity glass fiber filter was used, Gelman Spectroquality Type A. The filters were muffled to remove organics and have extremely low background levels of inorganics. They were tared by desiccating and weighing on consecutive days to a constant weight (±0.1 mg), and were then stored and handled throughout the tests and analyses in glass petri dishes.

- A solid sorbent trap, designed to adsorb the organic constituents in the sample gas stream, is located downstream of the heated filter and upstream of the first impinger. The sorbent trap, with overall dimensions of 170 x 45 mm, contained ~40 g of XAD-2, an Amberlite resin of the type commonly used as a chromatographic support.

- A Teflon valve was added to the glass connector between the sorbent trap and the first impinger through which glass bulbs were filled with the sample gas to be analyzed for any volatile or gaseous components not collected by the sorbent trap. This valve is also shown in Figure 4-13.

- For the C-5,6 test burns where large quantities of HCl were produced by combustion, a large, two-liter impinger (shown in Figure 4-13) was added between the solid sorbent trap and the first modified Greenburg-Smith (G-S) impinger. One liter of

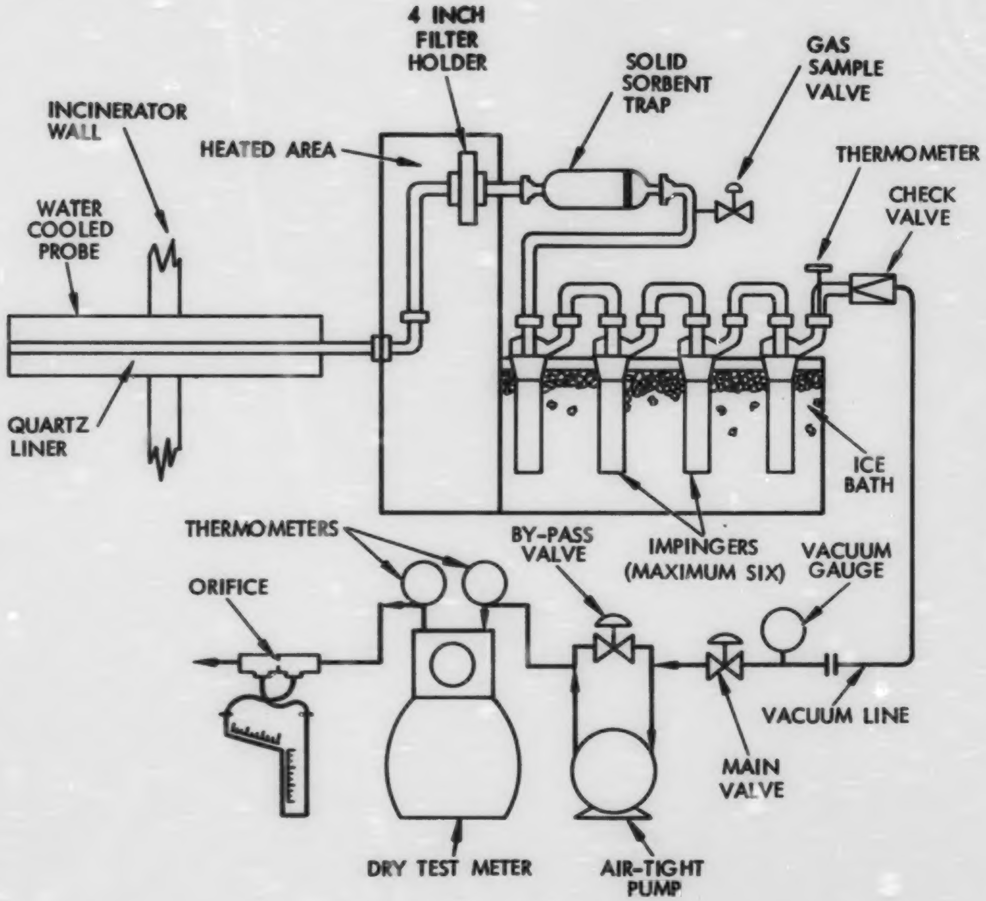
4 INCH FILTER HOLDER
SOLID SORBENT TRAP
GAS SAMPLE VALVE
INCINERATOR WALL
HEATED AREA
THERMOMETER
CHECK VALVE
WATER COOLED PROBE
QUARTZ LINER
ICE BATH
THERMOMETERS
BY-PASS VALVE
IMPINGERS (MAXIMUM SIX)
VACUUM GAUGE
ORIFICE
VACUUM LINE
MAIN VALVE
DRY TEST METER
AIR-TIGHT PUMP

Figure 4-12 Combustion Zone Sampling Train Schematic

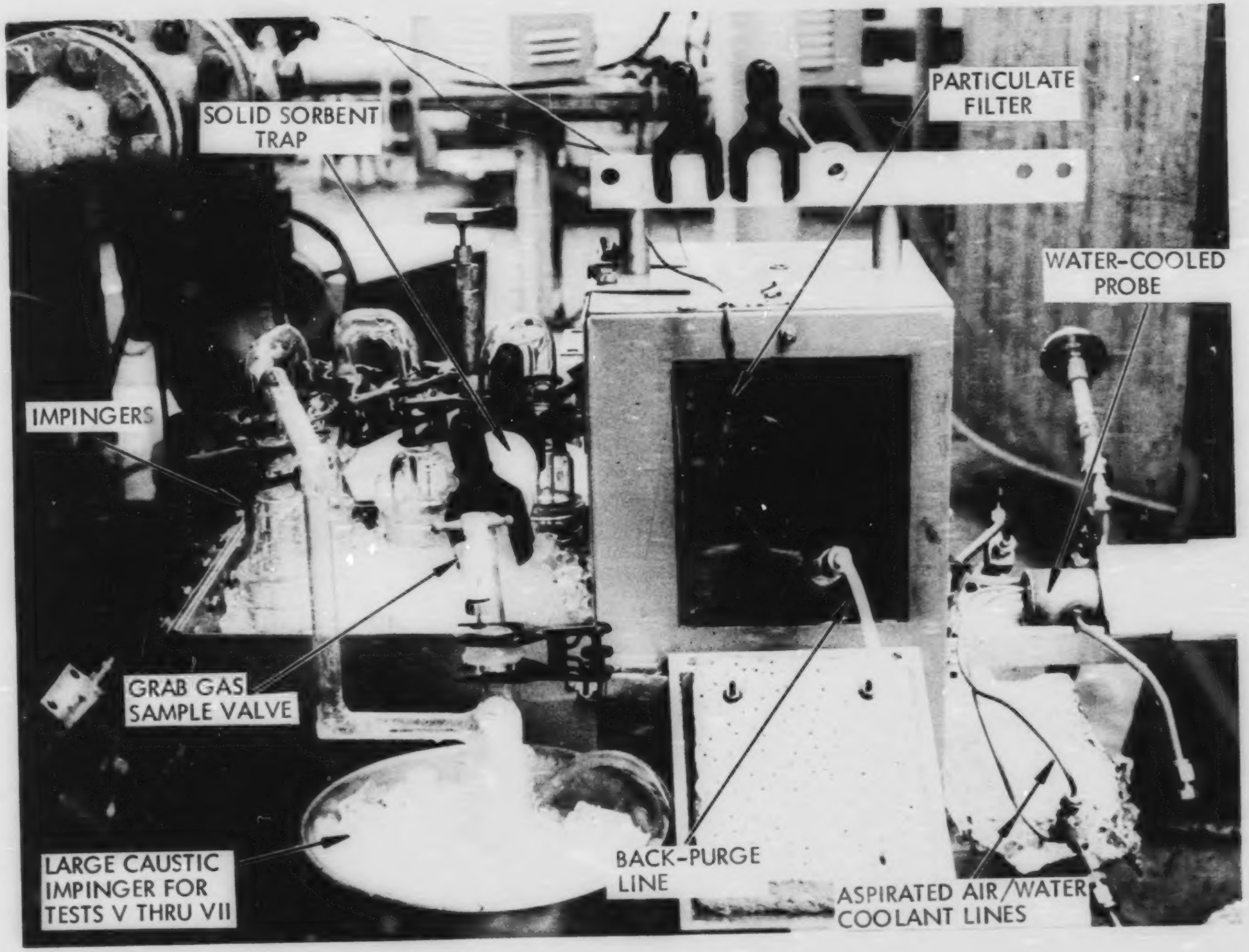
SOLID SORBENT TRAP
PARTICULATE FILTER
WATER-COOLED PROBE
IMPINGERS
GRAB GAS SAMPLE VALVE
LARGE CAUSTIC IMPINGER FOR TESTS V THRU VII
BACK-PURGE LINE
ASPIRATED AIR/WATER COOLANT LINES

Figure 4-13 Combustion Zone Sampling Train (Courtesy of the Marquardt Company)

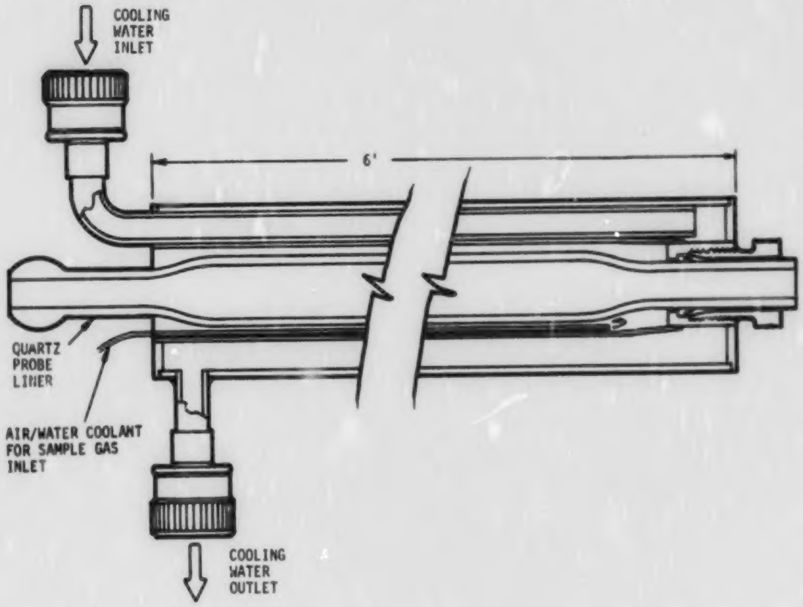

Figure 4-14 Water Cooled Probe Schematic

15 to 20 percent NaOH was placed in this large impinger in addition to 100 ml of 5 percent NaOH in each of the first two G-S impingers. The third impinger was empty and the fourth held silica gel. For the background No. 2 oil and ethylene waste tests, only distilled water was used in the first two G-S impingers.

This hot zone train was operated at a flow rate of approximately 30 liters/min for 3 hours during each test, thereby sampling an average of 4 to 5 cubic meters. Gas volumes were measured to 0.03 liter, with a leak rate of less than 0.6 liter/min. Operating parameters for the train and sample volume data are tabulated in Appendix B.

The following hot zone samples were obtained from each test:

- Solvent probe wash
- 10 cm diameter particulate filter
- Solid sorbent trap
- Grab gas
- Combined impinger solutions
- Acidified split of combined liquid impingers
- Spent silica gel

The location of the combustion zone sampling train at the test site is shown in Figure 4-15.

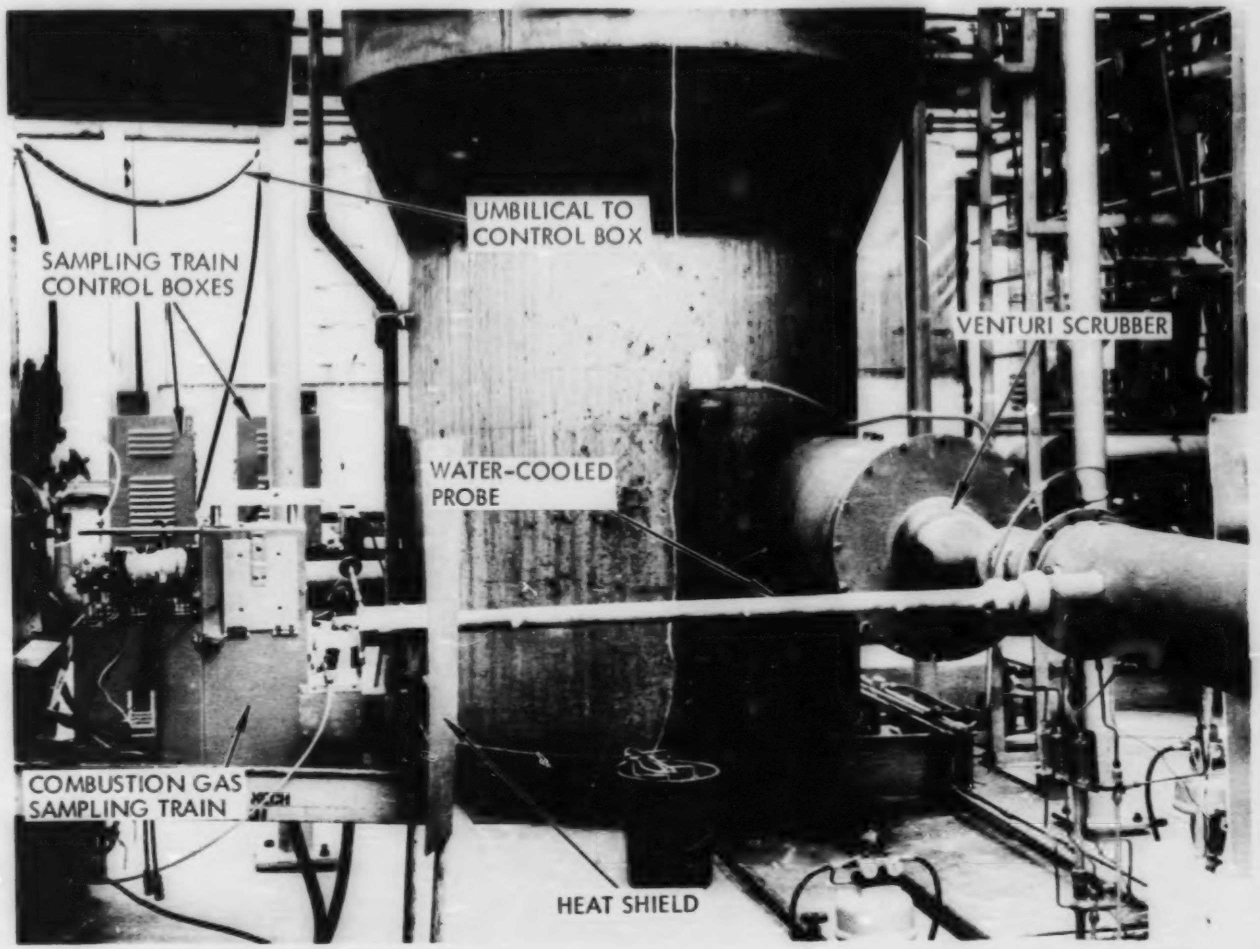
UMBILICAL TO CONTROL BOX
SAMPLING TRAIN CONTROL BOXES
VENTURI SCRUBBER
WATER-COOLED PROBE
COMBUSTION GAS SAMPLING TRAIN
HEAT SHIELD

Figure 4-15 Sampling System For Combustion Zone (Courtesy of the Marquardt Company)

4.3.3 Sampling Emissions and Waste Products

Samples of the stack effluent, spent scrubber water, and solid combustor residue (clinker), were taken during and after each test to evaluate the environmental safety of the final emissions. An EPA Method 5 test was performed at the stack for particulate mass loading and composition determinations. Location of the sampling train at the test site is shown in Figure 4-16. The standard train was used and two right angle, six-point traverses of the one-meter diameter stack were made, sampling for one hour at approximately 20 liters/min. It was decided at the start of the Marquardt tests that owing to the low velocity in the stack (6 to 8 ft/sec), the sample would be drawn superisokinetically in order to have an adequate particulate sample for compositional analyses. Gas volumes were measured to 0.03 liter, with a leak rate of less than 0.6 liter/min. Operating parameters for the train and sample volume data are tabulated in Appendix B.

The following samples were obtained for each test from the stack sampling train:

- Aqueous probe wash
- 10-cm diameter particulate filter
- Impinger solutions
- Acidified split of impinger solutions
- Spent silica gel

Gaseous stack effluents were determined by the use of Gastec® indicating absorbtion tubes. Toxic gases in ppm levels such as NO_x, SO_2, CL_2, HCl, and $COCl_2$ were looked for at the stack.

All of the spent scrubber water samples were obtained from a tap downstream of the tank which holds the water after it has passed through the venturi scrubber. Periodically during the test, as this water level rises, a pump removes the scrubber water from the tank and transfers it to a storage tank. It was during these pumping periods that composite samples were taken which make up the entire sample. The city water control sample was taken from a line which supplies water to the venturi scrubber. Whenver caustic scrubbing solutions are required in the scrubber, the caustic concentrate is blended with city water in a line leading to the venturi scrubber. No tap or sampling point was available in the line between the blending point and the venturi scrubber, hence, it was necessary to prepare the fresh caustic scrubber water control sample by blending the correct portions of concentrated caustic with city water. The mixing was performed within the one-gallon sample jug. Aliquots of these scrubber samples were acidified for subsequent metal analyses.

Samples of solid residue (or clinker) which accumulated in the combustor samples were collected when the burner assembly was removed after each test burn. The residue was then scraped out from the burner as completely as possible and wrapped in aluminum foil.

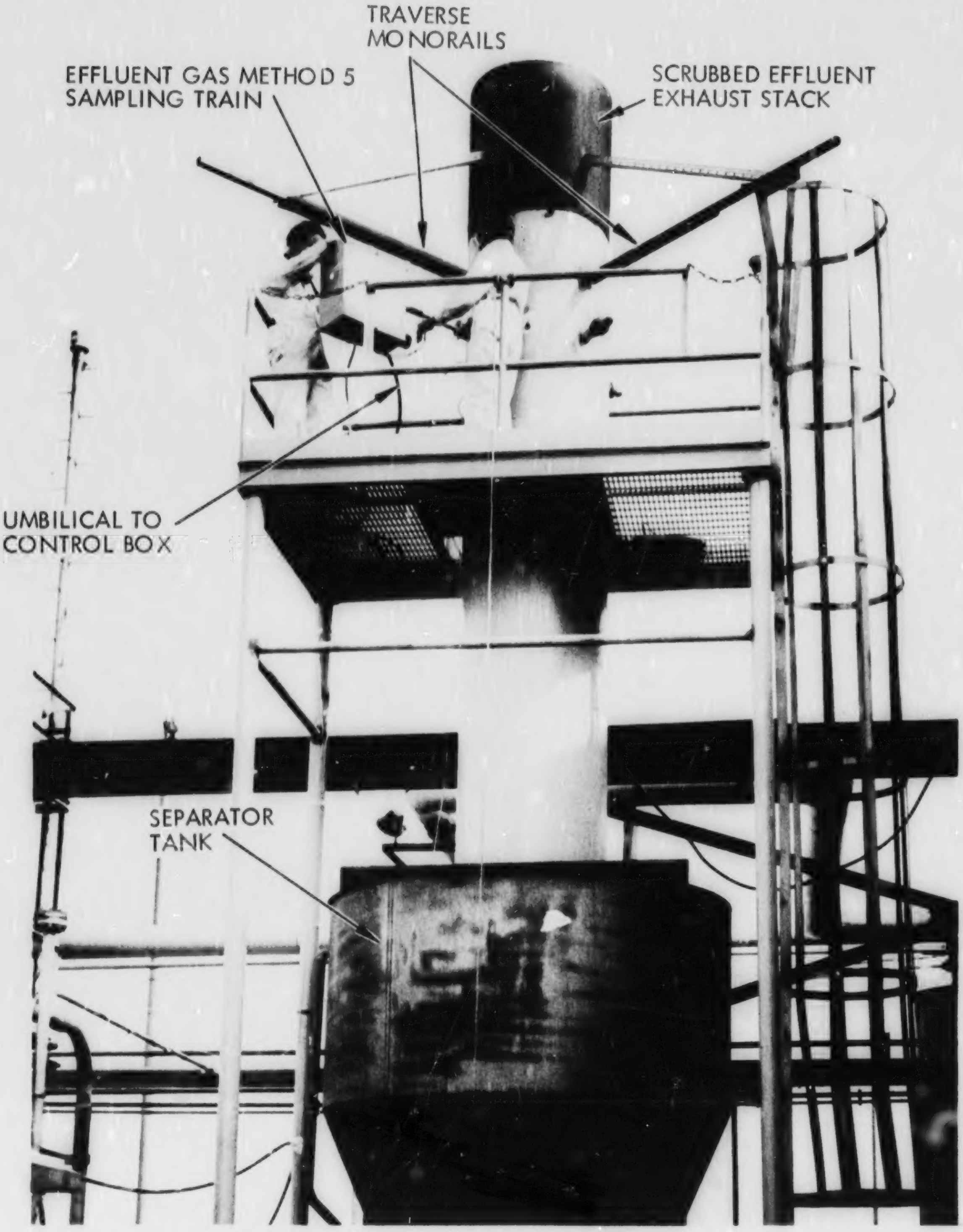
TRAVERSE MONORAILS
EFFLUENT GAS METHOD 5 SAMPLING TRAIN
SCRUBBED EFFLUENT EXHAUST STACK
UMBILICAL TO CONTROL BOX
SEPARATOR TANK

Figure 4-16 Sampling System For

Stack (Courtesy of the Marquardt Company)

4.4 ANALYSIS TECHNIQUES

Samples taken as described in Section 4.3, were analyzed for both organic and inorganic constituents. When necessary, extractions were performed first to concentrate the sample in a suitable form for analysis. Techniques used for these extractions and analyses will be briefly summarized here. For more detailed discussions, see the Marquardt Analytical Plan.

4.4.1 Extractions and Sample Preparation

Both solvents and acids were used to extract organics and inorganics respectively, from the appropriate samples. These procedures and the basic sample preparation steps are listed by sample type:

- Probe Washes

  Combustion Zone. The methylene chloride rinse was added directly to the filters after they were folded and placed in the Soxhlets for organic extraction (see filters below).

  Stack. The acetone probe rinse was evaporated and the residue weighed. This weight was added to the weight of the particulate on the filter for total mass loading calculations, in accordance with EPA Method 5 procedures.

- Filters

  Combustion Zone. The tared sample filters plus two controls were desiccated and weighed on consecutive days to a constant weight ±0.1 mg, and then extracted in a Soxhlet apparatus for 24 hours with methylene chloride. Solvent extracts were evaporated to 10 ml for analysis. Filters were then cut in half and one of the halves was weighed, low temperature plasma ashed, reweighed, and extracted with constant boiling aqua regia for two hours. This acid extract was reduced to 50 ml for analysis.

  Stack. The tared sample filters were weighed and cut in half. One of the halves was weighed, low temperature plasma ashed, reweighed, and extracted with constant boiling aqua regia for two hours. The acid extracts were reduced to 50 ml for analysis.

- Solid Sorbent Traps

  Combustion Zone. The XAD-2 resin was transferred from the traps to pre-extracted paper thimbles and then extracted in a Soxhlet apparatus with pentane and methanol for 24 hours with each solvent. These extracts were evaporated to 10 ml for analysis. Two unused traps were also extracted for background values and a blank (empty thimble) control was also run.

The original analysis plan had called for extraction of the sorbent traps with only one solvent, pentane. However, as discussed in Section 4.5.2, a second extraction with methanol was found to be necessary to remove the majority of material adsorped on the resin. In addition, the first set of traps to be extracted had even a third extraction with benzene. The benzene removed very little additional material and this third extraction was not continued through the remainder of the traps.

Stack. No solid sorbent traps were used in the stack sampling train.

- Grab Gas

Combustion Zone. No special preparation was required.

Stack. No gas samples were taken at the stack.

- Impingers

Combustion Zone and Stack. The volume of liquid in the impingers was measured and the spent silica gel was weighed in the field after each test burn to determine the amount of water collected. The impinger liquids from the combustion zone were also combined and a 100 to 250 ml aliquot acidified in the field to stabilize the metals for analysis. No extractions or other special preparation steps were performed on any of the impinger samples.

- Scrubber Waters

500 to 1000 ml aliquots of the scrubber water samples were extracted for organics according to the procedure for the separatory funnel extraction with Freon for oil and grease from water recommended by the EPA Handbook on Methods for Chemical Analyses of Water and Wastes (National Environmental Research Center, Cincinnati, Ohio, 45268, EPA-626-/6-74-003). However, instead of evaporating the material to the dried residue, the Freon extracts were concentrated to a 10 milliliter sample by use of a Kuderna-Danish concentrating evaporator. Aliquots of this 10 milliliter sample were then used for the survey analysis (IR and LRMS) and for gravimetric determination of residual material after evaporation at ambient conditions and immediate weighing.

- Solid Combustion Residues

The solid residues (clinkers) were first weighed, then ground and blended to provide a homogeneous sample. Ten to 20 g portions were extracted in a Soxhlet apparatus for 24 hours with methylene chloride. The solvent extracts were then evaporated to 10 ml for analysis.

4.4.2 Analytical Methods

After extraction of the samples for organic material and other preparation for inorganic material, the concentrated extracts, and aqueous solutions were analyzed by several methods which are summarized in Table 4-8. A general treatment of the sample preparation and analytical procedures is discussed below.

4.4.2.1 Organic Analyses

With the exception of the gas grab samples in glass bulbs, all of the samples for organic analysis were in 10 ml solvent extracts. Gas samples were analyzed on the Hitachi-Perkin-Elmer mass spectrometer. The samples were contained in double ended glass sampling vessels which have a septum through which syringe samples can be drawn. A gas tight syringe was used to remove part of the sample from the sample vessel and inject it into a heated stainless steel inlet system. The pressure of the sample in a constant volume portion of the inlet system was measured with a quartz manometer. Known pressures of helium and a 10.6 ppm propane standard were also introduced to the mass spectrometer (MS) for the purpose of background and calibration of instrument response. Tests samples were introduced to the MS with interspersed background samples to ensure that the instrument was not slowly accumulating a "memory" in the m/e peaks of interest.

The concentrated solvent extracts of the filters, sorbent traps, scrubber waters, and sand bed samples were analyzed by gravimetry, IR, LRMS and GC techniques. An aliquot of each extract was evaporated at ambient conditions to remove the solvent. The residue was weighed and analyzed by IR and LRMS.

The IR and LRMS analyses yield qualitative information about the classes or types of compounds (e.g., hydrocarbons, phenols, POMs, etc.) present as well as an idea of the complexity of the concentrated sample. Knowledge of the classes of compounds present provides a measure of the toxicity, if any, of the residue. The detection limits for these analytical techniques vary somewhat with the type of compound (see Table 4-8).

Two gas chromatograph systems were employed to cover the boiling point range of compounds which were expected in the samples if less than complete combustion were to occur. The first system described is for what are being called low boilers. This includes the very volatile solvents including methylene chloride, pentane and includes all of the compounds found in the ethylene waste with boiling points increasing up to but not including napthalene and ethylnaphthalene. These two compounds do in fact elute from this column system but with such long retention times that they are better analyzed with the second column system. The column system used for low boilers is as follows:

Column	Chromasorb 102,80/100 mesh, 6 ft x 1/8 inch
Temperature	200°C isothermal
Carrier Gas	helium at 30 cc/min
Detector	FID

Table 4-8 Summary of Analytical Methods

Method	Instrument Manufacturer and Model	Detectability for a Compound or Element Being Searched For
Organic Analyses		
Gravimetry	Mettler, microbalance	1 µg
Infrared Spectrophotometry (IR)	Perkin Elmer, 521	~ 3-5% of the sample being examined
Low Resolution Mass Spectrometry (LRMS)	Hitachi-Perkin Elmer, RMU-6 Mass Spectometer	~10 µg (1% of a 1 mg sample)
Gas Chromatography (GC)	Varian, 1860 dual FID	~100ng per µl of sample
Combined Gas Chromatography/Mass Spectrometry (GC/MS)	Varian, 1860 GC and Hitachi-Perkin Elmer, RMU-6 MS	~1 µg per µl of sample
	or	
	Finnigan, 9500 GC and Finnigan, 3100D Quadrapole Mass Spectrometer	~100 ng per µl of sample
Inorganic Analyses		
Inductively Coupled Plasma Optical Emission Spectrophotometry (ICPOES)	Applied Research Laboratories, QA-137	~0.5-2000 ppb
Atomic Absorption Spectrophotometry (AAS)	Jarrell Ash, 810	~1-0.001 ppm
Spark Source Mass Spectrophotography (SSMS)	AEI Scientific Apparatus Ltd., MS 702R	~50-100 ppb

The second column system used in the GC analysis was for what are called high boilers. These materials are defined as those which have the higher boiling points which begin around 200°C and increase from there. Napthalene is one of the first eluting compounds this system and the larger, higher boiling materials, such as POM, hydrocarbon oils etc., elute after napthalene. The operating parameters used for the GC separation of the high boilers follows. These two column systems combined were able to elute all the constituents found in both the wastes tested at TMC as well as possible incomplete combustion products or species formed in combustion.

Column	OV-225
Temperature	180°C isothermal
Carrier Gas	helium at 30 cc/min
Detector	FID

4.4.2.2 Inorganic Analyses

Inorganic analyses were performed using atomic absorption spectroscopy (AAS), optical emission spectroscopy (OES), and inductively coupled plasma optical emission spectroscopy (ICPOES). Selected samples of the acid extractions of the particulate filters and the acidified splits of the scrubber waters and the impingers were surveyed for trace metals by ICPOES.

The ICPOES analysis determines 32 elements, including most of the toxic elements of interest to the program, down to ppb levels with an accuracy of 100 to 200 percent. The purpose of this survey is primarily to check that the metals in these test samples are in approximately the same amounts relative to each other as they were in the waste material. Those elements which from the results either of the ICPOES survey or of the analysis of the waste material seemed to be present at potentially toxic levels, were determined quantitatively by AAS. The sensitivity of this method varies from approximately 1.0 to 0.001 ppm for the elements which were determined, with an accuracy between 10 to 50 percent.

In addition to the AAS and ICPOES analyses performed on the test samples, spark source mass spectrophotography (SSMS) was used to analyze the waste material for trace elements.

Some wet chemical methods were also performed on the combustion zone impinger solutions. Total available chlorine was determined by a ferrous ammonium sulfate titration, chloride by a modified Volhard tritration, and carbonate by evolution and gravimetry.

4.5 PROBLEMS ENCOUNTERED

Problems which occurred during either the field testing or laboratory analysis phases of the Marquardt test program are described in the following sections. Corrective actions taken and final disposition, when applicable, are also discussed.

4.5.1 Field Test Problems

In spite of careful selection of equipment and checkout at actual or simulated test conditions, a few incidents occurred during field testing that had not been anticipated. Corrective actions were immediately taken in each case, and testing was completed as scheduled. All necessary samples were acquired.

4.5.1.1 Inadequate Cooling of Combustion Gas Sample

Combustion gases at 1090°C or higher had to be cooled to 115°C or less at the entrance to the sampling train to avoid damage to the filter seals. A thermocouple in the gas stream at the entrance to the filter was used to monitor this temperature. Cooling of the sample gas was accomplished both by radiation from the quartz probe liner to the water-cooled probe (Figure 4-14) and by convective cooling with a stream of compressed air directed around the probe liner. Checkouts of this cooling method both in a boiler at TRW and during initial tests at TMC (TMC Run #1) were successful in maintaining a sample gas temperature of 220-230°F at the filter inlet. However, during the first sampling test (TMC Run #3), the sample gas temperature suddenly rose to 177°C at the filter inlet even after over an hour of steady-state operation had been completed with the temperature at this point well controlled at 105 to 110°C.

This problem was corrected by adding water as well as compressed air to cool the combustion gas. Facility air and water flow, controlled by metering valves, were mixed in a tee fitting and fed into a tube exiting along the quartz probe liner (Figure 4-14). Both air and water flows could then be precisely metered to control the sample gas temperature. Using this cooling method, sample gas temperature was maintained at safe levels of 80 to 105°C at the filter inlet for the remainder of the tests.

4.5.1.2 RAC® Train Modifications

The standard EPA Method 5 sampling trains ordered from Research Appliance Corporation required certain modifications before they could be used on this program. These modifications were completed before the start of actual sampling tests, so no schedule delays were involved.

First, the heated oven box enclosing the particulate filter was poorly insulated and sealed, making control of the internal temperature erratic. Next, the oven box fan took in cold outside air instead of recirculating the warm air within the box. This resulted in large thermal fluctuations and gradients.

Modifications to the sample train included re-insulating the heater box by removing the loose filter fiber glass matting and installing fire resistant 1.3-cm thick acoustic tiles to the interior of the box. Although the oven box blower motor had to remain outside of the heater box (because it could not withstand the internal temperature of nominally 120°C), the squirrel-cage blower itself was re-installed inside the box to recirculate only the heated air. These modifications greatly improved the control of oven box temperature by reducing thermal gradients and eliminating most of the heat losses.

4.5.1.3 HCl Corrosion of Hydrocarbon Analyzer

Examination of the analyzer components prior to testing made it apparent that the HC analyzer could not withstand continuous, long-duration exposures to moist, hot, HCl gas streams without significant damage to its brass and copper plumbing. The choice was then made to substitute a Perkin-Elmer 881 gas chromatograph with an open tubular column and FID for the Beckman instrument for monitoring hydrocarbon levels during the C-5,6 waste burns. The chromatograph's primarily stainless steel plumbing was less susceptible to HCl attack and could be operated intermittenly to further minimize its exposure to the corrosive sample stream.

4.5.1.4 Caustic Scrubbing of Acid Gases

The acid gas stream produced in the C-5,6 runs would also corrode the pump and gas meter in the sampling train control box. To protect these components and also to measure quantitatively the volume of HCl produced, a large, 2-liter impinger (shown in Figure 4-13) was added to the train. This impinger was filled with 100 to 1200 ml of 13 to 22 percent sodium hydroxide solution. A small amount of phenolphthalein was added to this impinger before each test run in order to visually be able to observe neutralization of the caustic solution.

Early neutralization did occur on the first test burn (TRW Run #V), causing sampling to be stopped after 2-1/4 hours. The premature exhaustion of the caustic solution was attributed to underestimating the effect of CO_2 being scrubbed out as sodium carbonate. On subsequent test runs, allowance was made for this factor and no further problems with the caustic impingers were encountered.

4.5.2 Laboratory Analysis Problems

4.5.2.1 Trace Metal Losses from Chlorinated Organic Wastes

It is not totally unexpected that it is proving difficult to obtain accurate and precise determinations, with a minimum detectability of 1 ppm, of the trace metals in the chlorinated, organic matrix of our waste materials. Of the techniques which can be performed on the neat sample, the detection limits of X-ray fluorescence range from 5 to 500 ppm; and chlorine is a major interferent with neutron activation analysis. Other techniques with good accuracy and sensitivity, such as SSMS, AAS, and ICPOES, require an ashed sample. During ashing, volatile metals and metal halides are lost which negates the quantitative capability of the analysis.

A set of comparative experiments is planned in order to evaluate special ashing and oxidizing procedures for trace metal retention. A commercially prepared standard containing 20 elements in fuel oil will be mixed with chlorinated organics to obtain an appropriate matrix. Techniques for analyzing the ash will in turn be compared using the optimum ashing and preparation methods selected.

4.5.2.2 Extraction of the Solid Sorbent Traps

Extraction of the collected samples from the solid sorbent traps was complicated by problems with the designed extractors. The extractor, shown in Figure 4-17 was fabricated so that the sorbent trap would fit between the upper and lower portions and distilled solvent would be continuously passed through the resin bed. The only difficulty was in obtaining a leak-free seal around the ball and socket joints. The best solution has turned out to be Teflon sleeves. Some were ordered, but were not received until late in the analysis schedule. With the Teflon sleeves, the designed extractors work well, and will be used for future test samples.

In the meantime, it was decided to use a standard Soxhlet apparatus. This technique involved pre-extracting paper thimbles, transfering the XAD-2 resin to the thimble, and then extracting the resin in the Soxhlet. The principle behind the two methods is the same. However, the Soxhlet method presents the question of background organic contributions from the thimbles.

4.5.2.3 Use of Multiple Solvents for Extractions

After completion of the initial pentane extraction of the first set of sorbent traps, the resin was observed to have remained considerably discolored. This discoloration was assumed to represent organic compounds still absorbed on the resin. Subsequent extraction of the traps with a polar solvent, methanol, removed five to six times more material by weight. These results showed that a single solvent extraction, even over a 24-hour period, would not remove those compounds which are only slightly soluble in the solvent. Proceeding with this new information, a third extraction was performed using benzene since this would be the best solvent for aromatics, chlorinated aromatics, and POMs. However these extracts contained insignificant amounts of material, showed no trace of any of the above compounds, and had high backgrounds due to the resin not having been precleaned with benzene. Consequently, the benzene extractions were not continued, and only pentane and methanol extracts were made of the remaining sorbent traps.

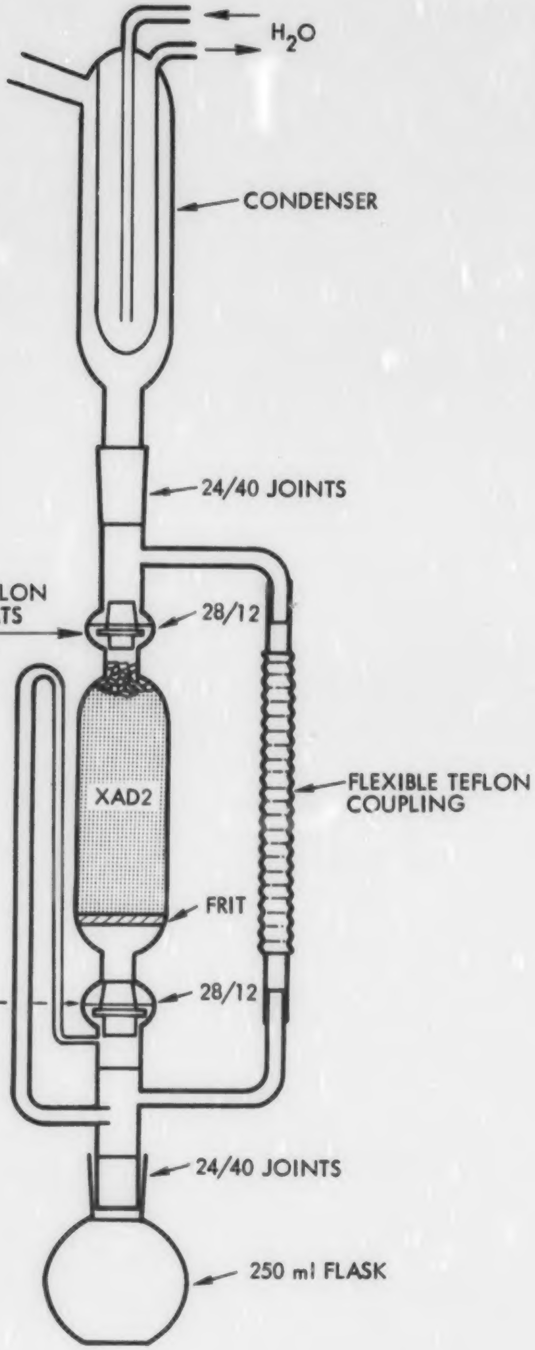
H_2O
CONDENSER
24/40 JOINTS
TEFLON SEATS
28/12
XAD2
FLEXIBLE TEFLON COUPLING
FRIT
28/12
24/40 JOINTS
250 ml FLASK

Figure 4-17. Sorbent Trap Extractor

5. TEST RESULTS

Test burns at The Marquardt Company (TMC) consisted of a background test with No. 2 fuel oil (MA-I), three tests with ethylene waste (MA-II, III, IV) and three tests with C-5,6/fuel oil blends (MA-V, VI, VII). This section presents results of analyses performed on these test samples. The section is divided into results for: 1) on-line combustion gas analysis, 2) waste destruction analysis, and 3) final emissions analysis which include stack gases, scrubber waters and burner head residues. Methods and procedures for the preparation and analysis of test samples can be found in Section 4.4.

5.1 COMBUSTION GAS DATA SUMMARY

Gas concentrations (by volume) as measured primarily by the on-line instruments are presented in Table 5-1. Other methods were used to quantify those species which were not measured by continuous monitors. Percent water was calculated according to EPA Method 4 using the volume of water collected in the combustion zone sampling train. To determine the mole percent of HCl and Cl_2 gases, chlorides and total available chlorine were titrated in the combustion zone sampling train caustic impinger solutions. In addition, SO_x gases were determined by Gastec® indicating tubes.

The data generally follow the operating parameters of the respective tests. The ethylene tests consisted of varying the waste and air feeds to achieve different combustion temperatures and therefore the CO_2, H_2O, and NO_x values rise along with increasing feed/temperature conditions. Due to the high sulfur content of the ethylene waste (1.32%) the resulting SO_x emissions could only be roughly estimated. SO_x levels were difficult to measure with the Gastec® tubes because the tubes were calibrated for 1 to 100 ppm.

The C-5,6 tests consisted of holding nominally constant feed rates while increasing the waste/auxiliary fuel ratio. This produced corresponding increases in the levels of HCl and Cl_2 while CO_2, NO_x, and SO_x levels remained essentially the same. The fairly constant level of CO throughout all seven tests indicates that good combustion was achieved at all tested conditions. The HC values are not believed to indicate significant differences betwen tests since: 1) readings were at the low range of the Beckman analyzer where its accuracy is somewhat poor, and 2) measurements were made non-redundantly with two different analyzers (Tests I to IV with the Beckman 402, and Tests V to VII with the gas chromatograph) so that the two sets of values cannot be directly compared.

5.2 WASTE DESTRUCTION ANALYSIS SUMMARY

Sampling of the combustion zone from the SUE® burner reaction tailpipe was accomplished just upstream of the venturi scrubber with the sampling train described in Section 4.3.2. The samples from the train consisted of a probe wash, filter, sorbent trap, grab gas sample and impinger liquids. These samples were then separated into their organic and inorganic constituents and analyzed by appropriate techniques, as described in Section 4.4. Analysis of the combustion products is aimed

Table 5-1. Total Gas Composition in the Combustion Zone by Volume

Run No. and Fuel Description	O_2 (%)	CO_2 (%)	N_2 (5)	H_2O (5)	HCl (%)	Cl_2 (ppm)	CO (ppm)	NO_x (ppm)	HC (ppm)	SO_2 (ppm)
Fuel Oil Background										
I	6.3	9.8	73.0	10.9	-	-	12	170	10	15-20
Ethylene Waste										
II	7.2	10.3	74.0	8.5	-	-	17	200	5-10	100-200
III	9.4	9.3	73.4	7.9	-	-	17	150	5-15	100-200
IV	4.9	11.5	74.2	9.4	-	-	22	520	5	100-200
C-5,6 Fuel Oil										
V	8.1	8.4	69.6	12.7	1.15	<0.05	20	145	10-25	5
VI	5.6	9.7	68.8	14.2	1.64	15	17	140	35-65	6
VII	5.5	9.5	67.9	14.7	2.35	56	17	120	30-35	5

mainly at identifying and quantifying any unburned waste or hazardous partial combustion products. The production of potentially toxic levels of trace metals from burning these wastes is also examined. Where quantified species are calculated in mg/m^3 in the sample gas stream, the gas volume data used to make these calculations are summarized in Appendix B. The level of interest for this program is defined as 0.1 mg/m^3 of sample gas, which represents the threshold level of the bulk of the most toxic species as defined by OSHA and other health and safety organizations.

5.2.1 Organic Composition

The organic analyses were divided into: 1) quantitative searches by gas chromatography for uncombusted constituents from the waste material or other specific compounds that could be expected to be present, and 2) qualitative surveys to identify unexpected compounds.

5.2.1.1 Results of Quantitative Analyses

The results of the gas chromatographic analyses on the extracts of the combustion zone filter and sorbent trap samples are presented in Table 5-2. The table shows that benzene, known to be present in the ethylene waste, and mesityl oxide (identified subsequently by GC/MS) were found in the combustion zone filter extracts. Mesityl oxide (4-methyl-3-pentene-2-one), an industrial solvent and rust remover, was found in MA-IV. It is likely an artifact of contamination during sampling or sample preparation.

Results of the analysis of the sorbent trap extracts by gas chromatography indicated that a total of five compounds are present in the seven sorbent trap extracts. Chromatograph retention times for these compounds did not coincide with retention times for the waste constituents thus no identification could be made on that basis. These compounds were arbitrarily identified as Compounds A through E based on chromatographic retention time. Their concentration levels, based on equal detector response, are presented in Table 5-2. Each sample had at least one of these compounds and six samples had two or more. Combined GC/MS was used to help resolve the composition of the extracts and identify the five unknown compounds. Four samples were selected for GC/MS in such a way that all five unknowns were contained in at least one of the selected samples.

Results of the GC/MS analysis indicated the presence of compounds predominantly silicones and oxygenated organics. None of the representative waste constituents were found in these sorbent trap extracts. No further analyses were performed on these samples since: 1) they are not part of the original composition waste, 2) they represent low ppm levels in the sample gases, and 3) there is no evidence of toxic characteristics in what is known of the compounds.

5.2.1.2 Qualitative Survey Analysis

Samples were surveyed by gravimetric, infrared spectrometry (IR), and low resolution mass spectrometry (LRMS) techniques. Since the qualitative results correlate more to sample type than to waste burn, the data are discussed in the following order:

Table 5-2. Results of Gas Chromatographic Analysis

Run Number and Fuel Description	Sample Gas Volume (m^3)	Filter Samples			Sorbent Trap Samples		
		Compound	Amount Found (mg)	Concentration of Detected Compounds (mg/m^3)	Compound (Note 2)	Amount Found mg	Concentration of Detected Compounds (mg/m^3)
Fuel Oil Background							
MA-I	5.28	Benzene	1	0.2	Compound A Compound B	14 1	3 0.2
Ethylene Waste							
MA-II	5.20	(Note 1)	None Detected Above Background	< 0.2	Compound A Compound B	20 1	4 0.2
MA-III	4.80	(Note 1)	" "	<0.2	Compound A Compound B Compound C	14 1 0.4	3 0.2
MA-IV	5.07	Mesityl Oxide	12	2.4	Compound A Compound C Compound D Compound E	3 0.8 0.4 1	0.6 0.2 0.1 0.2
C-5,6/Fuel Oil							
MA-V	4.15	(Note 1)	None Detected Above Background	<0.2	Compound A Compound C Compound E	0.4 0.1 1	0.1 <0.1 0.2
MA-VI	5.53	Benzene	3	0.5	Compound C	0.2	<0.1
MA-VII	4.54	Benzene	3	0.7	Compound C Compound D Compound E	3 0.5 1.5	0.6 0.1 0.3

NOTES

1. Benzene, in actuality, was found in all filter extracts, including the filter blank. Those samples reported as having benzene have levels which exceed the control.
2. Five compounds, A to E have been detected based on retention times from the GC analysis. Further work to identify these compounds is discussed in Section 5.2.1.

a. Combined particulate filter and probe wash extracts

b. Sorbent trap extracts

c. Grab gas samples

a. Combined Probe Wash and Particulate Filter Extracts

The combustion zone filters were extracted with methylene chloride using the procedures described in Section 4. Table 5-3 presents the amount of residues found in the combustion zone filter extracts and the resulting concentrations in the sampled gas. The values have been corrected for the amount of material extracted from the control, an unused filter. The amount of material found after extraction of the control filter was only somewhat less than that found on each of the sample filters and its qualitative nature was also similar. This is indicative of low level contamination which often plagues trace organic analysis, even though these filters were fired in a muffle furnace carefully preconditioned, handled in clean glassware, and extracted with chromatographic grade solvent.

The extractable organic material from the combustion zone filters analyzed by IR and LRMS consisted of alkyl hydrocarbons and alkyl esters of phthalic acid which are not considered toxic. No evidence of any of the starting toxic materials was seen. No additional effort was made to fully identify the esters and/or hydrocarbons present. A detailed discussion of observations made during preparation of the filters is found in Appendix D.

Table 5-3. Organic Material Extracted From Combustion Zone Filters

Run No.	Amount of Material Extracted (mg)	Sample Gas Volume, Wet Basis (m^3) at 1 atm and 21°C	Concentration Level in Gas (mg/m^3)
Fuel Oil Background			
I	0.80	5.28	0.15
Ethylene Waste			
II	0.55	5.20	0.11
III	0.65	4.80	0.14
IV	4.40	5.07	0.87
C-5,6 Fuel Oil			
V	1.50	4.15	0.36
VI	1.55	5.53	0.28
VII	1.35	4.54	0.30

b. Sorbent Traps

This section presents the results of the survey analyses performed on the extracts of the sorbent traps from the combustion zone sampling train. The amounts of organic materials found by extraction and gravimetry in the samples are presented in Table 5-4.

Examination of the IR and LRMS data leads to the conclusion that certain classes of compounds commonly used as processing aids and found in many industrial products and processes are present. There is evidence to believe these compounds are indeed present in the combustion gases, but were also found in the control and blank samples which were never exposed to combustion gases. Details of control and blank analyses are provided in Appendix D.

Table 5-4 shows that significant amounts of extractable materials were found and at levels considerably higher in the sample traps than the unused sorbent trap which was used as a control. The IR and LRMS data indicated hydrocarbon oils or greases, fatty acid compounds and phthalic acid esters. The amounts of these materials found in the sample traps are so much greater than the amounts found in the several control experiments that either or both of the following conclusions must be reached: 1) these species were actually present in the combustion gases, or 2) they were originally in the sorbent trap resins despite prior clean up, and the exposure to conditions inherent during sampling somehow aids in their release from the resin matrix and subsequent solvent extraction.

Table 5-4. Organic Material Extracted From Sorbent Traps, Survey Analysis

Sample	Amount of Material Extracted (Corrected for Control) (mg)	Sample Gas Volume, Wet Basis (m^3 @ 1 atm and 21°C)	Concentration Level in Sample Gas (mg/m^3)
MA-I-CG-ST	60.67	5.28	11.5
MA-II-CG-ST	49.49	5.20	9.5
MA-III-CG-ST	70.32	4.80	14.6
MA-IV-CG-ST	100.86	5.07	19.9
MA-V-CG-ST	92.60	4.15	22.3
MA-VI-CG-ST	133.58	5.53	24.2
MA-VII-CG-ST	119.76	4.54	26.4
Control (Unused Sorbent Trap)	7.36	4.00 Assigned	1.8

c. Grab Gas Samples

Grab gas samples were taken from the combustion zone sampling train downstream of the sorbent trap during train operation. Analysis of these grab gas samples for possible organic species passing through the solid sorbent traps was performed by LRMS. Inspection of the mass spectra indicates that only propane and butane were present in the samples at rather constant levels which never exceeded 10 ppm. No other organic materials were present in the sample. The calculated lower limit of detection for other compounds of similar organic composition under the same analytical conditions is 2 ppm. Table 5-5 summarizes the results of the analysis. The levels are reported as ppm propane since a propane standard was used to determine mass spectrometer response factors.

Table 5-5. Analysis of Organics in Grab Gas Samples

Sample	Organic Content (ppm as Propane)
MA-I-CG-GG	9
MA-II-CG-GG	9
MA-III-CG-GG	9
MA-IV-CG-GG	9
MA-V-CG-GG	9
MA-V-HA-GG	8
MA-VI-CG-GG	9
MA-VI-HA-GG	9
MA-VII-CG-GG	9
MA-VII-HA-GG	8

Those samples with the designation "CG" in their labels were taken from the sampling valve downstream of the sorbent trap in the combustion zone sampling train. Those with a "HA" were taken downstream of the gas chromatograph which was being used as a total hydrocarbon analyzer during the last three runs with the chlorinated waste.

5.2.2 Inorganic Characterization

Inorganic elemental concentrations were determined by analysis of the particulate filters and aqueous impinger samples. The filters were first weighed to determine total particulate loading. The loadings obtained are reported in Appendix D, Section D.7, along with other weights taken at subsequent steps of filter preparation for analysis.

After total particulate weights were measured, the combustion zone filters were solvent extracted for organic species and the filters were then photographed. Figure 5-1 shows a photograph of the particulate filters obtained from sampling the combustion gases from Tests I through VII, in order going from left to right and top to bottom. The sooty nature of the filters from the C-5,6 tests agrees with observations made during these three tests that relatively larger amounts of burner residue (clinker) were being formed. The clinker itself is described in Section 5.3.3. The irregular dark and light markings on the filters shown in the photograph are the result of prior folding of the filters for solvent extraction.

Trace metals on the particulate filters were put into solution by acid digestion of the filters. The liquid collected in the impingers was combined into one sample and an aliquot of that was acidified for trace metal analyses. The filter digests and acidified impinger solutions from Tests I (No. 2 background), IV (ethylene waste), and VI (C-5,6 waste) were surveyed semi-quantitatively by inductively coupled argon plasma optical emission spectrometry (ICPOES).

Quantitative analysis for selected elements were then performed by atomic absorption spectrometry (AAS) on all samples. The elements to be analyzed were selected by the following criteria:

1. Potentially toxic (e.g., Pb, Cd, Sb, and Hg)
2. Present at significant levels as determined by the: survey analysis of the wastes (Section 4.1), and/or survey analysis of the filter acid digests and impinger solutions.

Using these criteria, four elements were selected for AAS analysis, Cr, Pb, Co, and Sb. Although not among the most toxic of metals, Cu, Zn and Mn were also analyzed for an additional comparison of the ICPOES and AAS results. The ICPOES analysis indicated only very low levels of any toxic elements (see Appendix D, Section D.8), which is confirmed by the AAS results shown in Table 5-6, with the exception of the element Pb. Results from analysis of the stack samples are also included in this table for purposes of comparison.

In those cases where elements were either not detected or were measured at levels less than or equal to background levels, a less than value is given. As expected, metal concentrations are fairly constant for Runs II, III, and IV in which the ethylene waste was fed at approximately the same rate for each test. On the other hand, for Runs V, VI, and VII, in which the C-5, 6 was was fed at increasingly higher concentrations, a

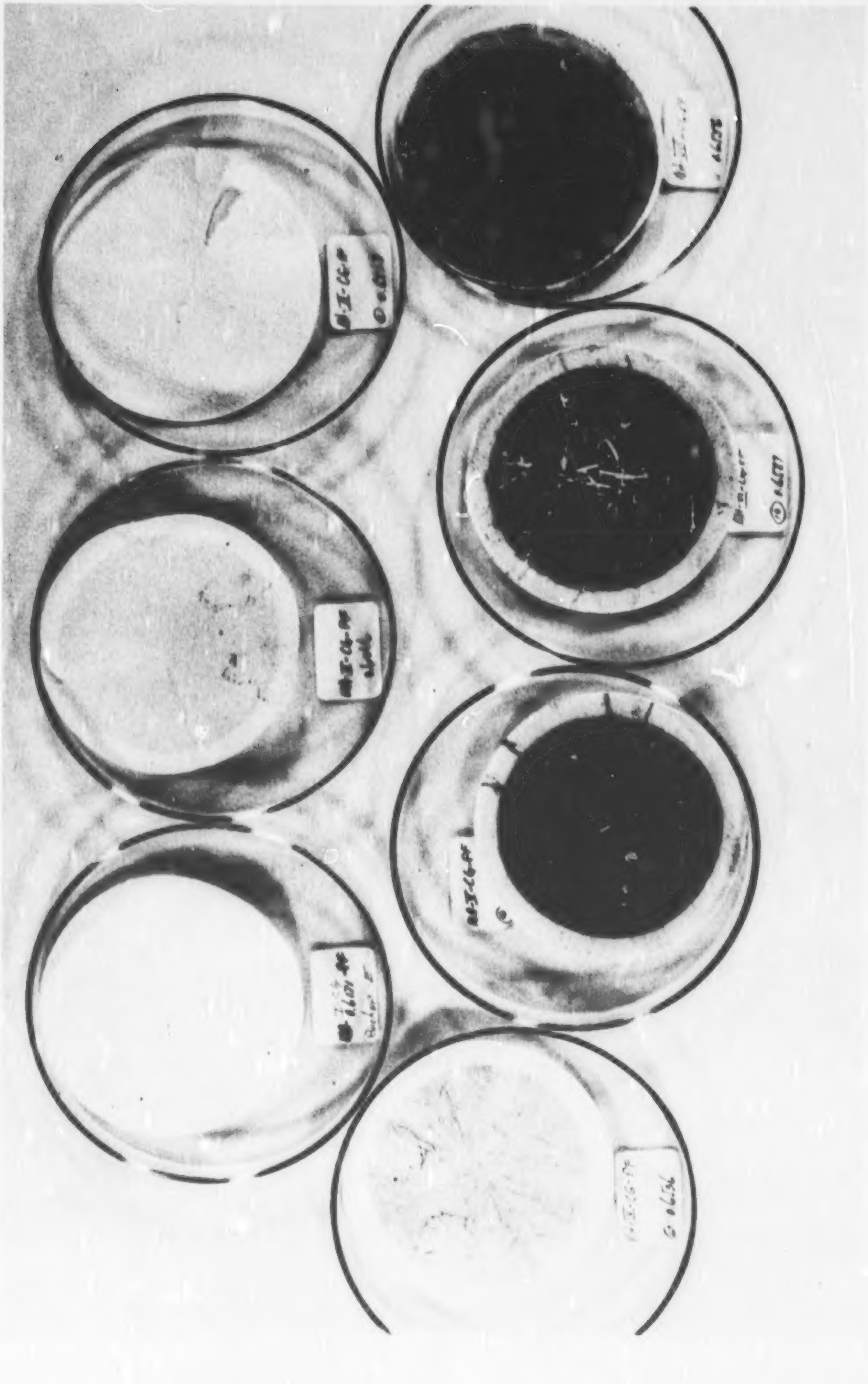

Figure 5-1. Filters From Combustion Zone Gas Sampling After Solvent Extraction

Table 5-6. Toxic Trace Metals at Level of Interest (mg/m^3) by AAS

	Copper		Chromium		Lead		Zinc		Manganese		Cobalt		Antimony	
	Impingers	Filter	Impingers	Filter	Impingers	Filter	Impingers	Filter	Impingers	Filter	Impingers	Filter	Impingers	Filter
Run I														
Stack	-	NGTB <0.003	-	ND <0.001	-	0.001	-	NGTB <0.2	-	NGTB <0.001	-	-	-	-
Combustion zone	0.022	NGTB <0.001	ND <0.001	ND <0.001	0.002	0.002	0.005	NGTB <0.008	0.001	NGTB <0.001	-	-	-	-
Run II														
Stack	-	NGTB <0.001	-	ND <0.001	-	0.001	-	NGTB <0.05	-	NGTB <0.001	-	-	-	-
Combustion zone	0.022	0.002	ND <0.001	0.003	0.003	0.003	0.009	NGTB <0.06	0.001	0.001	-	-	-	-
Run III														
Stack	-	NGTB <0.001	-	ND <0.001	-	0.001	-	NGTB <0.1	-	NGTB <0.001	-	-	-	-
Combustion zone	0.021	0.002	ND <0.001	NGTB <0.001	ND <0.001	0.002	0.010	NGTB <0.007	0.001	NGTB <0.001	-	-	-	-
Run IV														
Stack	-	NGTB <0.005	-	ND <0.001	-	0.003	-	NGTB <0.07	-	NGTB <0.002	-	-	-	-
Combustion zone	0.021	0.002	ND <0.001	0.001	0.002	0.002	0.011	NGTB <0.008	0.001	0.003	-	-	-	-
Run V														
Stack	-	0.014	-	0.008	0.01	0.003	-	NGTB <0.3	-	0.034	-	0.003	-	NGTB <0.008
Combustion zone	0.071	0.015	0.002	0.030	0.55	0.010	0.023	NGTB <0.03	0.077	0.025	0.090	0.003	0.007	NGTB <0.003
Run VI														
Stack	-	0.008	-	0.014	0.01	0.005	-	NGTB <0.4	-	0.065	-	0.003	-	NGTB <0.005
Combustion zone	0.086	0.008	0.001	0.045	0.95	0.006	0.006	NGTB <0.02	0.12	0.067	0.19	0.004	0.008	NGTB <0.002
Run VII														
Stack	-	0.022	-	0.037	0.05	0.006	-	NGTB <0.2	-	0.17	-	0.011	-	NGTB <0.009
Combustion zone	0.059	0.013	0.001	0.14	1.40	0.008	0.008	NGTB <0.02	0.19	0.10	0.33	0.007	0.007	NGTB <0.003

NGTB - Not greater than background

ND - Not detected

corresponding rise in the level of metals emitted can be seen. Of the metals analyzed by AAS, only chromium is trapped predominently on the filter, which substantiates the need for careful metal analysis of the impinger solutions.

In addition to the trace metal analyses, the impinger solutions from the C-5,6 tests were also analyzed by wet chemical methods for the HCl, Cl_2, and CO_2 scrubbed from the combustion gases by the caustic in the impingers. The volumes of HCl and CO_2 were needed in order to correct the gas sample volumes as measured by the dry gas meter. The levels of free chlorine, a potentially toxic specie, were determined to be <0.005, 15, and 56 ppm for Tests V, VI, and VII, respectively. Complete results of these wet chemical analyses are described in Appendix D, Section D-8.

5.3 Final Emissions

The stack gas, scrubber water and burner head residue (clinker) that make up the final emissions from the SUE® burner incineration system were sampled during each test and analyzed to determine the environmental safety of the tests at TMC.

5.3.1 Stack Gases

Stack effluents were sampled during the tests with both a standard EPA Method 5 train and Gastec® detection tubes. The Method 5 train was used to obtain samples for the determination of particulate loading and elemental composition of the particulate, and the Gastec® tubes were used to measure potentially hazardous gaseous species such as hydrocarbons, HCl, Cl_2, and $COCl_2$.

5.3.1.1 Samples Obtained From the Method 5 Train

The particulate filters obtained from sampling the stack gas are shown in Figure 5-2. The filters from Tests I through VII are presented in order going from left to right and top to bottom.

Particulate mass loading was determined by adding the weight of particulate found on the filter to the weight of the residue obtained by evaporating the probe washes to dryness. This gross weight is then corrected for the appropriate blank or control values and divided by the total gas sample volume. The resulting values, in both metric and English units, for the particulate emitted from the stack are presented in Table 5-7.

After weighing, the filters were acid digested and selected samples were surveyed for trace metals by inductively coupled argon plasma optical emission spectroscopy (ICPOES). The ICPOES results (presented in Appendix D, Section D.8) indicated very low levels of all toxic elements as did the quantitative analyses by atomic absorption spectrometry (AAS) presented in Table 5-6. Because of the relatively high level of lead and its predominante collection in the impingers from the combustion gas, lead was also determined in the stack impingers and found to be quite low.

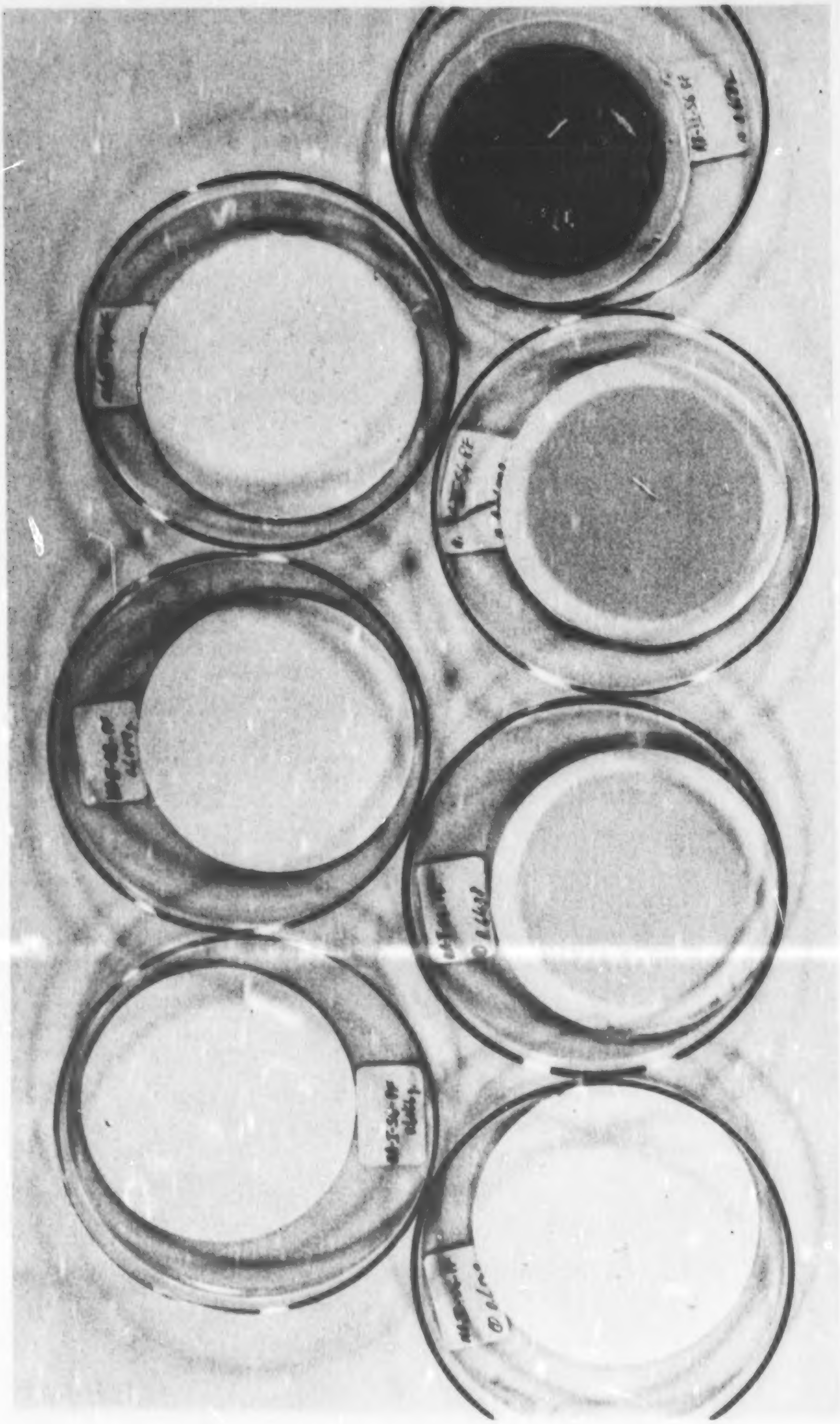

Figure 5-2. Filters From Stack Gas Sampling

Table 5-7. Particulate Mass Loadings

Test No.	Particulate Loading	
	Mg/m^3	Grains/Std. Ft^3
I	21.2	0.0092
II	20.9	0.0091
III	25.0	0.0109
IV	20.4	0.0089
V	36.2	0.0158
VI	43.8	0.0192
VII	113.5	0.0494

In addition to the seven elements discussed in Table 5-6, the element sodium was also determined by AAS in the digests of the stack filters from the C-5,6 runs since it was suspected that the relatively high weights on these samples were due to NaCl produced by the caustic scrubber. Indeed, if all the Na measured (after correction for the background of the control filters) is assumed to be present as NaCl, the weight of NaCl accounts for 85 to 90 percent of the stack particulate, as shown in Table 5-8. This calculation is probably a good average since the values for the weight of sodium salts would be higher for any sodium carbonate present and lower for any sodium hydroxide present.

5.3.1.2 Gastec® Tube Measurements

Gastec® detection tubes were used to analyze for low concentration gases that could be present. Sulfur oxides were measured in this way and these results reported in Table 5-1. Other gases which were checked using Gastec® tubes were HCl, Cl_2, $COCl_2$, and hydrocarbons. Within the specified limits of detection, none of these gases as listed in Table 5-9, were found to be present.

5.3.2 Scrubber Waters

The scrubber water samples were obtained by compositing the spent liquid as it was pumped off during each test burn. A sample of the city water and the concentrated caustic solution blended with city water for the C-5,6 tests were also taken for background measurements. Aliquots of these samples, with the exception of the city water, were acidified for subsequent metal analyses.

Table 5-8. Percent Sodium Salts as NaCl on Stack Filters

Run No.	Total Wt. of Material on Filter (mg)	Wt. of Na Recovery by Acid Digestion (mg)	Wt. Sodium Salts as NaCl (mg)	Percent NaCl of Particulate on Filter (mg)
V	38.1	13.0	33.04	87
VI	93.9	33.5	85.14	91
VII	139.4	46.50	118.18	85

Table 5-9. Gastec® Tube Results

Sampling Location	Run No.	Detector Tube	Limits of Detection
Stack	All	Gasoline (aliphatic)	<0.005 percent
Stack	V, VI and VII	HCl Cl_2 $COCl_2$	<0.2 ppm <0.33 ppm <0.1 ppm
Gas Chromatograph[a] Outlet	V, VI and VII	$CoCl_2$	<0.1 ppm

[a] The only practical opportunity for testing the combustion zone gases with Gastec® tubes to check for any production of phosgene was at the outlet of the GC sample bypass line. The GC, as previously mentioned, was substituted for the Beckman HC monitor during the C-5,6 runs.

5.3.2.1 Organic Characterization

Quantitative

The various scrubber water samples were extracted with Freon to remove and analyze the organic materials in them. The concentrated extracts were then analyzed by gas chromatography. The results are summarized in Table 5-10.

Table 5-10. Results of Gas Chromatographic Analysis of Scrubber Water Samples

Run Number	Scrubber Water			
	Volume of Scrubber Water Extracted (Liters)	Low Boiling Material in Scrubber Water Extract (mg)[a]	Higher Boiling Material in Scrubber Water Extract (mg)[a]	Concentration of Extracted Material in Scrubber Water (mg/l)
Fuel Oil Background				
I	1.00	26	0.7	27
Ethylene Waste				
II	1.00	73	0.8	74
III	0.50	30	0.4	61
IV	1.00	28	0.5	28
C-5,6/Fuel Oil				
V	0.50	60	<0.1	120
VI	1.00	20	<0.1	20
VII	1.00	26	<0.1	26
City Water Control	1.00	53	<0.1	53
Fresh Caustic Water Control	1.00	12	<0.1	12

---

[a] See Section 4.4.2 for definition of low boiling and higher boiling materials. Instrument response (calibration) for low and higher boilers was determined with standard injections of benzene and naphthalene respectively.

No evidence of the ethylene waste or C-5,6 waste constituents were found in the chromatographic data. The levels reported in Table 5-10 represent three artifacts that are present in the control samples and the fuel oil background samples as well as the test samples. It can be reasonably concluded that these materials are not generated as a result of burning waste.

Qualitative Survey

An aliquot of the concentrated organic extract from the scrubber water samples was also subjected to the survey analysis for unexpected combustion by-products etc. The results of the gravimetric determination of the residue is presented in Table 5-11. A trend of changing organic content in the scrubber water than the No. 2 oil baseline burn or the ethylene waste burns. The premature shutdown of Test VII test is not believed to have caused the higher value for the scrubber water extract sample. Instead the low values associated with Runs V and VI, are considered to be inconsistently low.

Table 5-11. Results of Analysis of Concentrated Organic Extracts of Scrubber Water Samples

Sample	Volume of Scrubber Water Extracted (liters)	Amount of Extracted Material by Gravimetry (milligrams)	Concentration in Scrubber Water, mg/liter
City Water[a]	1.00	0.53	0.5
Fuel Oil Background			
MA-I-SW	1.00	84.42	84.4
Ethylene Waste			
MA-II-SW	1.00	70.0	70.0
MA-III-SW	0.50	62.0	124.0
MA-IV-SW	1.00	77.1	77.1
Control			
MA-V-FSW[b]	1.00	16.3	16.3
C-5,6/Fuel Oil			
MA-V-SW	0.50	0.9	1.8
MA-VI-SW	1.00	0.7	0.7
MA-VII-SW	1.00	33.2	33.2

[a] City water was used as the wet scrubber feed for Tests MA-I through MA-IV. This sample is therefore the control sample for the first four tests.

[b] A control sample of fresh caustic scrubber solution was prepared by blending concentrated caustic with city water according to the blending proportions used for Test MA-V. Therefore, this sample is the control for tests MA-V through MA-VII.

Survey analyses by infrared spectrophotometry (IR) and low resolution mass spectrometry (LRMS) were performed on the residues obtained from the evaporation of the Freon solvent in which the residues were dissolved. The IR data for all the scrubber water extract samples were all extremely similar, and while no evidence of the waste constituents were seen, the spectro indicated hydrocarbon oils, greases, fatty acid esters. The LRMS data supported the IR findings but also detected minor amounts of phthalate esters.

5.3.2.2 Inorganic Characterization

The scrubber water samples, aliquots of which had been acidified in the field, were analyzed by AAS for several elements of interest. Identified for analysis as a result of being detected in the representative waste samples were Cu, Cr, Pb, Zn, Mn. Cobalt (Co) an antimony (Sb) were found in the combustion test samples and were added to the test matrix. The results of those analyses, corrected for appropriate background are presented in Table 5-12.

The Los Angeles County Sanitation District Phase I concentration limits for point source discharge to a sewer were consulted. These heavy metal concentrations are all at least a factor of ten below the most stringent maximum allowable concentration for these listed metals which is 10 mg/liter (ppm). It is concluded that these scrubber waster were sewered in accordance with local regulations.

Table 5-12. Elemental Analysis of Scrubber Water by AAS (ppm)

Run No.	Cu	Cr	Pb	Zn	Mn	Co	Sb
I	0.10	0.21	0.08	0.37	0.48	---	---
II	0.11	0.29	0.02	0.82	0.42	---	---
III	0.07	0.01	0.02	0.12	0.06	---	---
IV	0.13	0.38	0.02	0.74	0.59	---	---
V	0.15	0.18	0.21	0.23	0.19	0.051	0.18
VI	0.14	0.18	0.31	0.21	0.12	0.074	0.22
VII	0.23	0.35	0.54	0.17	0.23	0.12	0.24

5.3.3 Solid Residues

The solid residue (clinker) samples were obtained when the burner head was opened after each test burn. The clinker was then scraped off the burner head as completely as possible and wrapped in aluminum foil. The quantities obtained were as follows:

Fuel Oil	
Run I	None (probably <50g)
Ethylene Waste	
Run II	295g
Run III	245g
Run IV	533g
C-5,6/Fuel Oil	
Run V	662g
Run VI	2327g
Run VII	1480g

It must be noted, however, that these weights in no way represent the total weight of clinker produced in each burn. There was evidence from both feed pressure readings and acoustic observations that the clinker tended to build up, break off, and travel down the tail pipe through the scrubber. In fact, on the last run (VII), the tip of the mullite probe at the end of the tailpipe for the on-line instruments was believed to be broken by clinker hitting it.

The clinkers were analyzed in duplicate by a micro-analytical combustion technique for their carbon and hydrogen content. The black, powdery, coke-like appearance of the clinkers indicated that they would probably be 95 to 99 percent elemental carbon. The micro analysis results, shown in Table 5-13, supported this conclusions.

Table 5-13. C and H Analysis of Clinkers

Element	Run II	Run III	Run IV	Run V	Run VI	Run VII
Percent Carbon	98.46	97.07	99.30	88.90	97.27	98.02
Percent Hydrogen	0.61	0.79	0.52	1.19	0.40	0.40
Total	99.07	97.86	99.82	90.09	97.67	98.42

5.3.3.1 Organic Analysis

Portions of the clinker from each test were extracted for organics with methylene chloride solvent in a Soxhlet extractor. The extract was further prepared for analysis using the procedures in Section 4.4. The concentrated extracts were analyzed by GC for waste constituents as well as other unexpected by-products. The survey analysis, gravimetry, IR, LRMS were also applied to the extracts.

Quantitative

The results of the GC analysis of the clinker extracts for the runs with ethylene wastes are presented in Table 5-14. It shows that detectable amounts of extractable material were present in the clinker from MA-II, MA-III and MA-IV. Furthermore, the retention times on the gas chromatograms for the sample extracts are the same as those of the ethylene waste representative sample. It is concluded that uncombusted ethylene waste is present in the clinker at the levels shown in Table 5-14. This is borne out by the IR and LRMS survey analysis on the same extracts which also indicated residuals of the original waste. Two compounds were found by GC to be present in the clinker extracts from the C-5,6 tests (Table 5-14). The retention times for the two peaks do not coincide with retention times for any of the compounds in the representative sample of C-5,6 which was chromatographed under the same conditions. Further work to identify these two peaks present at these relatively low levels was not carried out since LRMS and IR of the clinker from these tests (discussed next) did not indicate the presence of any chlorinated hydrocarbon species.

Survey

Aliquots of the concentrated clinker extracts were mildly evaporated and the residues subjected to gravimetry, IR and LRMS. The amount of residue obtained after mild evaporation of the clinker extracts are presented in Table 5-15. The ethylene test clinkers clearly have more extractables than the C-5,6 clinker.

Inspection of the IR spectra of the clinker extracts from the tests with the ethylene manufacturing wastes (Runs II, III and IV) revealed that all three samples contain aliphatic and aromatic hydrocarbons. Comparison of these spectra with that of the waste feed indicates that uncombusted or incompletely combusted waste feed is present in the clinker. The clinker has a strong odor characteristics of dicyclopentadiene, a constituent of the waste.

The LRMS data for the clinker extracts from the ethylene waste tests Runs II, III and IV also indicate the presence of alkyl substituted naphthalenes and cyclohexadiene. There is no evidence of any polynuclear aromatic hydrocarbons larger than naphthalene.

The IR and LRMS survey analyses of the clinker extracts from the C-5,6 tests (Runs V, VI and VII) showed that the three samples have essentially the same composition. The IR spectra indicate that these extracts were all aliphatic hydrocarbons, the source of which was likely the auxiliary fuel that was mixed with the C-5,6 waste prior to burning. The clinker extract

Table 5-14. Results of Analysis of Clinker Extracts by Gas Chromatography

Run Number and Fuel Description	Weight of Clinker Sample Extracted (g)	Low Boiling Material in Clinker Extract (mg)[a]	Higher Boiling Material in Clinker Extract (mg)[a]	Concentration of Extracted Material in Clinker (mg/g Clinker)	Comments
Fuel Oil Background					
I	NOT APPLICABLE NO CLINKER RECOVERED				
Ethylene Waste					
II	10.360	25	0.5	2.4	Extracted materials were identified as ethylene waste constituents
III	9.102	16	0.8	1.9	
IV	15.654	27	0.8	1.8	
C-5,6/ Fuel Oil					
V	13.166	11	<0.1	0.8	Extracted materials not identified as C-5,6 waste constituents
VI	15.160	8	<0.1	0.5	
VII	14.110	14	<0.1	1.0	

[a] See Section 4.4.2 for definition of low boiling and higher boiling materials. Instrument response (calibration) for low and high boilers was determined with standard injections of benzene and maphthalene respectively.

Table 5-15. Residue Extracted from Clinker

	Ethylene			C-5,6		
	Run II	Run III	Run IV	Run V	Run VI	Run VII
$\frac{\text{mg extracted}}{\text{g clinker}}$	4.73	21.12	3.71	0.52	0.28	0.15

from MA-VII also contained eitheraldehydes, ketones, esters, or possibly a mixture of them as shown by IR. Neither the IR nor the LRMS data show any trace of C-5,6 similar chlorinated species, or POM. The level of detection of the IR for these materials was experimentally determined to be about 5 percent in the extractables.

Samples of this solid clinkers themselves were also directly examined by LRMS (no extraction) before and after they were solvent extracted. The following observations were made:

- The ethylene waste test clinkers contained the waste constituents confirming the GC analysis. Examination of the solvent extracted clinker by the same LRMS technique showed only a trace organic content. The extraction of the clinker was thus estimated to be more than 95 percent complete based upon mass spectrometer instrument response.

- The unextracted clinker from the C-5,6 tests contained benzene and/or toluene, aliphatic hydrocarbons, and monatomic and diatomic chlorine combustion products. Hexachlorocyclopentadiene (C-5,6) and other chlorinated organics were specifically searched for, but no trace of any chlorinated compounds were detected in the unextracted clinker. Levels of detection are estimated at 0.1 and 1 percent of the clinker. In addition, the typical 149 AMU peak for phthalate esters was found in all of these C-5,6 clinker samples. This is significant because these clinker samples were not extracted or otherwise processed except for grinding, and the probability of contamination during grinding is very small indeed. Thus, the presence of phthalates in the clinker is strong evidence for the presence of phthalates in C-5,6 waste/fuel oil feed used in the tests. This can exaplain the presence of at least part, if not all, of these phthalates in the samples from C-5,6 testing. Examination of the extracted clinker showed only traces of hydrocarbon pickets and methylene chloride, indicating an extraction efficiency similar to that found for the ethylene test clinkers.

5.3.3.2 Inorganic Analysis

Samples of the clinkers were also analyzed by optical emission spectroscopy (OES) for elemental inorganic composition. The results of this analysis are presented in Table 5-16.

Certain other elements whose presence was indicated in the representative samples by analysis (see Section 4) were, in turn not detected by OES. Table 5-17 presents these elements of interest and their limits of detection below which they would not be seen by OES when present in a carbon matrix similar to the clinker.

Table 5-16. Inorganic Composition of Clinkers (ppm)

Element	Run II	Run III	Run IV	Run V	Run VI	Run VII
Al	30	100	100	30	30	30
B	10	100	50	10	30	30
Ca	10	20	50	20	10	10
Cr	300	10	100	10	30	30
Cu	5	100	50	5	10	5
Fe	1000	200	3000	70	30	100
Pb	20	30	30	50	10	10
Mg	50	800	800	30	30	30
Mn	10	10	20	ND*	10	10
Ni	200	ND**	1000	ND**	ND**	ND**
Si	50	500	500	10	20	20
Na	ND***	ND***	ND***	2000	ND***	ND***

*<5 ppm

**<10 ppm

***<100 ppm

Table 5-17. OES Detection Limits

Element	Estimated Detection Limit (ppm)
As	100
Ba	500
Co*	5
Hg	1000
Sb*	50
V*	30
Zn	200

* Would only be likely to be present in C-5,6 test samples (Runs V, VI and VII).

6. WASTE INCINERATION COST

Individual economic analyses were performed to determine the costs of incinerating, on an industrial basis, the annual source plant productions of the two waste materials tested at The Marquardt Company (TMC). The economic analyses were divided into capital investment and annual operating costs. The economic analysis for each disposal facility, for the SUE® incinerator and scrubbing system portion, was based on equipment prices, estimates of manpower requirements, and fuel and power consumptions obtained from TMC. The costs of other portions of the disposal facilities and associated labor were estimated using the Happel Method, data from Guthrie ("Capital Cost Estimating", Chemical Engineering, March 24, 1969) and standard engineering reference methods. Equipment costs were adjusted to January 1976 prices using the Marshall Steven Cost Indexes. Land prices and transportation costs are not included in the two disposal plant cost estimates. Both incineration plants are assumed to be at the manufacturing plant generating the waste to be disposed.

6.1 CAPITAL INVESTMENT

The capital investment for the facility to incinerate 15 million kilograms per year of ethylene manufacturing wastes shown in Table 6-1 is based upon a design concept which employs in parallel one 1500 liters/hour (400 GPH) and one 760 liters/hour (200 GPH) SUE® burner-incinerator-scrubber system, fed by a common automatic feed system. The facility costs include, as common use items, an ethylene manufacturing waste storage tank (16 hour storage capacity), a scrubbing water supply system (24-hour storage capacity), and a settling pond with a 24-hour retention capacity. It was assumed that the only fuel needed for the incinerators was the ethylene manufacturing wastes.

The size of the facility was based on a ninety percent plant operating factor and 15 million kilograms per year of ethylene wastes with a density of 910 g/liter. The 2270 liters/hr, ethylene wastes incineration plant has a nominal capacity of 10 percent over the required capacity of 2070 liters/hr.

The total capital investment for the ethylene manufacturing waste incineration facility is estimated at $1,818,000. It should be noted that over one-third of this capital investment is directly due to scrubbing equipment and scrubbing related facilities which may not be required for incinerating a fuel as "clean" as the ethylene manufacturing wastes tested.

The capital investment for the plant required to incinerate 4.5 million kilograms per year of the hexachlorocyclopentadiene wastes mixture shown in Table 6-2 is based on sizing the incinerator conservatively on the heat of combustion resulting from feeding a 1:2 weight ratio of C_5Cl_6 waste and No. 2 fuel oil. This is equivalent in size to a 1500 liters/hr (400 GPH) SUE ® burner incinerator. The plant design concept includes the associated scrubber system, an automated feed system, a C_5Cl_6 waste storage tank (with 24-hour storage), a No. 2 fuel oil storage tank (24-hour storage), and the caustic soda solution storage tank (24-hour capacity). Auxiliary equipment

Table 6-1. Capital Investment

15 Million kg./Yr. Ethylene Manufacturing Waste Incineration Plant

Equipment	Size	Estimated Costs Equipment	Labor
1-SUE ® Basic incinerator, with scrubbing system *	2,270 LPH	272,750	
1-Ethylene Manufacturing Waste Storage Tank system	33,300 liters	11,500	
1-Scrubbing Water Supply System - Tank	2,650,000 liters	100,000	
- Pumps	8,950 -17,900 watts		
1-Automated feed system, waste		50,000	
1-Scrubber Wastes Collection Settling Pond	2,650,000 liters	20,000	
		454,250	45,425
Piping (at 45%)		225,000	225,000
Foundations (4%)		20,000	30,000
Buildings (4%)		20,000	14,000
Structures (4%)		20,000	4,000
Fire Protection (0.75%)		3,750	22,500
Electrical (4.5%)		22,500	32,500
Painting & Cleanup (0.75%)		3,750	22,500
		769,250	395,925
Material & Labor	$1,165,175		
Overhead (30%)	350,000		
Total Erected Cost (130%)	1,515,000		
Engineering Fee (10% erected)	151,500		
Contingency Fee (10% Erected)	151,500		
Total Capital Investment	$1,818,000		

* Includes burner, incinerator, reaction tailpipe, Venturi scrubber, scrubber tank, pump, air supply system, waste pump.

Table 6-2. Capital Investment
4.5 Million kg./Yr. Hexachlorocyclopentadiene Waste Incineration Plant

Equipment	Size	Estimated Costs Equipment	Labor
1-SUE Ⓡ Basic incinerator, with scrubbing system*	1,500 LPH	171,250	
1-C_5Cl_6 Waste Storage Tank, Heated, SS	7,950 liters	22,500	
1-No. 2 Fuel Oil Storage Tank (& Pump)	31,400 gal	10,000	
1-Scrubbing Water Supply System-Tank -Pump	1,890,000 liters 17,900 watts	80,000	
1-50% Caustic Soda Storage Tank & Pump	22,710 liters	8,300	
1-Automated feed system, waste & oil		100,000	
1-20% HCl** Storage tank & pump, rubberlined	16,870 liters	12,200	
1-pH Control System, scrubber pond		10,000	
1-Scrubber Wastes Collection & Settling Pond	1,890,000 liters	15,000	
		429,500	43,000
Piping (45%)		193,300	193,300
Foundations (4%)		17,200	25,800
Buildings (4%)		17,200	12,000
Structures (4%)		17,200	3,500
Fire Protection (0.75%)		3,200	19,500
Electrical (4.5%)		19,300	28,000
Painting & Cleanup (0.75%)		3,200	19,200
		700,100	344,300
Material & Labor	$1,044,400		
Overheat (30%)	313,300		
Total Erected Cost (130%)	1,358,000		
Engineering Fee (10%)	136,000		
Contingency (10%)	136,000		
Total Capital Investment	$1,630,000		

*Includes burner, incinerator, reaction tailpipe, Venturi scrubber, scrubber tank, pump, air supply system, waste pump.

** From plant waste HCl.

also includes the scrubbing water supply system tank (24-hour capacity) and pump, the scrubber wastes collection/settling pond (24-hour storage), the pH control system, and the storage tank (24-hour capacity) for the plant waste HCl used to adjust pH.

The estimated capital investment for the C_5Cl_6 waste mixture is $1,630,000. This estimate, as noted above, is conservative since the tests at TMC showed that only a 1:1 feed ratio between waste and No. 2 fuel oil was required to achieve satisfactory incineration.

6.2 ANNUAL OPERATING COSTS

The annual operating costs consist of annual labor, chemical and utility costs plus cost of capital, equipment depreciation, maintenance, taxes and insurance. The labor costs have been calculated on the number of personnel assigned to operate the incinerator and the automatic waste loading equipment at rates prevalent in the chemical industry. The costs for supervision, supplies and payroll-related expense are also included.

The utility costs include electricity and scrubber water; solid waste disposal costs are shown separately. In the plant for hexachlorocyclopentadiene waste incineration, the costs shown also include the annual requirements for No. 2 fuel oil and sodium hydroxide. The amount of No. 2 fuel oil consumed was based on a 1:1 weight ratio with C_5Cl_6 wastes (shown to have proper incineration characteristics by tests at TMC). Annual electricity usage was based on estimates from TMC. Scrubber water and caustic soda requirements were calculated from plant test data.

The annual operating costs for the plant to incinerate 15 million kilograms per year of ethylene manufacturing wastes are summarized in Table 6-3. The estimated annual operating expense for this plant is $1,037,500 or $69.31/metric ton. As noted earlier for "Capital Investment", approximately one-third of this annual cost for the disposal of ethylene wastes is due to scrubber-associated systems which may not be mandatory in this case.

The annual operating costs for the plant to incinerate 4.5 million kilograms per year of hexachlorocyclopentadiene wastes are summarized in Table 6-4. The estimated annual expense based on hexachlorocyclopentadiene wastes is $2,211,700 or $487.59/metric ton.

Both disposal plant annual cost estimates were premised on 24-hour per day operation, 330 days per year. The "cost of capital" shown is based on the assumption that private debt financing is used for each disposal plant.

Table 6-3. Annual Operating Cost
15 Million kg./Yr. Ethylene Manufacturing Waste Incineration Plant

Item			Cost - $/Yr.
Depreciation (15% of plant investment)			272,700
Cost of Capital (10% of plant investment)			181,800
Maintenance (8% of plant investment)			145,400
Utilities			86,400
Electric power 290KW(7920) ($0.015)		= 34,500	
Scrubber water 787 x 10^7 liters/yr @ $0.066/1000 liters		= 51,900	
Solid Waste disposal @ 6.50/metric ton for 2% wt. processed = $\frac{15 \times 10^6}{1000}$ (.02) ($6.50) = 2,000			2,000
Labor			312,800
Incinerator Operator	1 x 24 x 365 x $7.50	= 184,000	
Incinerator Operator Helper	1 x 24 x 365 x $6.50		
Automatic Feed System Operator	1 x 24 x 365 x $7.00		
Supervision (15% Operating Labor)		= 27,600	
Supplies (20% Operating Labor)		= 36,800	
Payroll Related Expense (35% Labor)		= 64,400	
Taxes & Insurance @ 2% Plant Investment			36,400
		Total	$1,037,500

Cost per metric ton of ethylene manufacturing waste = $69.31

Table 6-4. Annual Operating Cost
4.5 Million kg./Yr. Hexachlorocyclopentadiene Waste Incineration Plant

Item		Cost - \$/Yr.
Depreciation (15% of plant investment)		244,500
Cost of Capital (10% of plant investment)		163,000
Maintenance (8% of plant investment)		130,400
Utilities		60,400
Electric power 190KW(7920) (\$0.015)	= 22,600	
Scrubber water 572 x 10^7 liters/yr @ \$0.066/1000 liters	= 37,800	
Supplies, Chemical		1,266,000
Fuel Oil, No. 2, 4.5 x 10^6 kg = 32,530 bbl@ \$13.00/bbl	= 423,000	
NaOH (50% solution) 5.35 x 10^6 kg @ \$158 metric ton	= 843,000	
HCl - Plant waste at zero value, 10.2 x 10^6 kg		
Solid Waste Disposal @ 5.90/ton for 2% of waste processed		2,000
Labor		312,800
Incinerator Operator 1 x 24 x 365 x \$7.50 Incinerator Operator Helper 1 x 24 x 365 x \$6.50 Automatic Feed System Operator 1 x 24 x 365 x \$7.00	=184,000	
Supervision (15% labor)	= 27,600	
Supplies(20% labor)	= 36,800	
Payroll Related Expense (35% labor)	= 64,400	
Taxes & Insurance @ 2% of Plant Investment		32,600
Total		\$2,211,700
Cost per metric ton of C_5Cl_6 waste	=\$487.59	

APPENDIX A

ASSESSMENT OF ENVIRONMENTAL IMPACT OF DESTRUCTING CHEMICAL WASTES AT THE MARQUARDT COMPANY

ASSESSMENT OF ENVIRONMENTAL IMPACT OF DESTRUCTING CHEMICAL WASTES

AT
THE MARQUARDT COMPANY
16555 SATICOY STREET
VAN NUYS, CALIFORNIA

The Marquardt liquid injection incinerator, located in Van Nuys, California, is adjacent to the Van Nuys Municipal Airport. This incinerator will be used for the destruction and evaluation of the following wastes:

1) Ethylene manufacturing waste

2) Hexachlorocylcopentadiene (C-5,6)

The Los Angeles Air Pollution Control District has been notified of the intent to thermally destruct these wastes at the Marquardt facility. The incinerator is operated under L.A. APCD Permit No. P55506.

The SUE® (SUdden Expension) burner, derived from aerospace engine technology, has demonstrated high effectiveness in incinerating waste propellants and solvents as well as chlorinated hydrocarbon herbicides and pesticides. The burner was designed for a continuous feed rate of 50 to 60 gallons per hour of liquid wastes, and a maximum wall temperature of 3000°F. TMC's incinerator facility is a well-instrumented research type installation equipped with a high energy venturi scrubber for control of atmospheric emissions. Scrubber water is analyzed by TMC personnel before discharge to the municipal water treatment system. Solid residue is disposed of in an approved landfill after analysis by TMC.

The area surrounding the incinerator facility includes other Marquardt test areas, the Van Nuys airport, and residential areas. The nearest residential area is a trailer court approximately 400 yards from the incinerator. Prevailing winds are from the west (toward the airport runways) at usually moderate velocity. The parking lot and nearby residential streets are lined with trees. No wildlife was observed in the immediate area.

Local vehicular traffic is not affected by this program, since drums are delivered only at the start of the test series. Operation of the incinerator is not noisy compared to other equipment, such as ramjets, tested at TMC. Only a white steam plume from the wet scrubber can be observed when the incinerator is operating. The incinerator facility operates 8 hours per pay only when tests are scheduled. A test crew consists of four to five persons.

The potential detrimental environmental effects are expected to result from: 1) storage and handling of wastes prior to destruction, 2) emissions occurring during tests, and 3) disposal of liquid and solid residue remaining after combustion. The most significant hazard would result from contact with waste liquid and/or fumes during a spill. The polymeric oil waste from ethylene manufacture has physical characteristics (viscosity, density, color) and elemental composition (88.7% C, 8.61% H, 1.32% S) similar to the No. 2

oil. The principal hazard of this waste is its flammability. The C_5Cl_6 waste contains approximately 56 percent C_5Cl_6, 33 percent octachlorocyclopentene (C_5Cl_8), and a number of other chlorinated cyclic compounds. C_5Cl_6 is known to be moderately toxic by ingestion, inhalation or through skin contact. The 1973 Toxic Substances List provides the following data on C_5Cl_6:

Oral Toxicity (rat): LD_{50} - 505 mg/kg

Dermal Toxicity (rabbit): lowest lethal dose - 430 mg/kg

Inhalation Toxicity:

LC_{50} (rat) - 3.1 ppm (3hr)

Lowest lethal dose (mouse) - 1.4 ppm (3 hr)

Lowest lethal dose (rabbit) - 1.4 ppm (3 hr)

LC_{50} (guinea pig) - 3.2 ppm (7 hr)

Toxicity data on C_5Cl_8 are not available. The toxicity of C_5Cl_8 is probably in the same range as C_5Cl_6.

Storage and Handling

TMC has established safety procedures for handling hazardous materials, including propellants and explosive materials. A detailed safety plan has been prepared for this program, including waste handling procedures. Wastes will be received by truck in 55-gallon drums, which will be inspected for leaks and stored in a bonded area until transferred into the run tank. All transfer operations will be conducted within a diked, electrically grounded area by trained personnel using appropriate equipment and protective clothing. Any leaks or spills will be flushed and incinerated.

Incineration Tests

Operating temperature and residence time of the liquid injection incinerator should provide essentially complete combustion of the wastes, resulting in harmless exhaust emissions. On-line monitoring of gases from the combustion zone will be utilized as an indication of combustion efficiency. In addition, stack emissions (downstream of scrubber) will be checked for hazardous gaseous species using Gastec® analyzer tubes for specific gases and vapors. Caustic scrubbing solution will be used for chlorine removal.

Disposal of Residue

Residue material from the incineration process will consist of scrubber water and ash. Liquid residue from the scrubber will be analyzed before discharge to the municipal water treatment plant by TMC personnel. Solid residues (ash) will also be tested by the TMC personnel prior to approved landfill. Wastes remaining in the storage/run tanks and wash down liquids from any spills will be incinerated at the conclusion of the test program.

APPENDIX B

SAMPLE TRAIN OPERATION AND SAMPLE VOLUME DATA

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APPENDIX B

SAMPLE TRAIN OPERATION AND SAMPLE VOLUME DATA

For each test, data was collected on the operation of the two sampling trains. This information is presented in Table B-1. The percent of isokinetic at which the gas samples were drawn from both the stack and combustion zone sampling sites was calculated from the following equation given in EPA Method 5:

$$I = \frac{\left(1.677\,\frac{\text{min}}{\text{sec}}\right)\left[\left(0.00267\,\frac{\text{in. Hg-cu ft}}{\text{ml - }^{o}\text{R}}\right) V_w + \frac{V_m}{T_m}\left(P_{bar} + \frac{H}{13.6}\right)\right] T_s}{eV_sP_s\,\left(\frac{.7854\ D_n^2}{144}\right)}$$

The terms of this equation are defined, and values measured for each test burn are summarized in Table B-1. It was assumed for the purpose of these calculations that P_s at the stack was nearly ambient or slightly positive, and that the 0.5-inch diameter combustion zone probe would behave roughly like a 0.5-inch nozzle.

Tables B-2 and B-3 summarize the sample gas and collected water volume data.

TABLE B-1. GAS VOLUME DATA

Weights/Conditions	Run I		Run II		Run III		Run IV		Run V		Run VI		Run VII	
	SG	CG	SG	CG	SG	CG	SG	CG	SG	CG	SG	CG	SG	CG
Volumes at Standard Conditions (ft^3)														
V_{meter}	62.71	170.87	64.68	172.57	47.72	160.22	46.84	166.65	46.76	129.72	82.99	169.04	45.75	136.29
V_{water}	46.93	15.64	30.62	11.00	24.65	9.10	33.75	12.23	30.15	14.98	39.72	22.75	31.19	19.55
V_{Cl_2}										0.000		0.003		0.009
V_{HCl}										1.686		3.205		3.758
V_{CO_2} scrubbed										---*		0.276		0.576
Mole Fractions														
B_{water}	.452	.109	.347	.085	.366	.079	.444	.093	.417	.127	.349	.142	.430	.147
B_{Cl_2}										.000		.000		.000
B_{HCl}										.012		.016		.024
Gas Molecular Weight (lb/lb-mole)														
M_{dry}	30.05	30.05	30.11	30.11	30.02	30.02	30.25	30.25	29.94	30.02	30.09	30.19	30.10	30.25
M_{wet}	24.63	28.74	25.91	29.08	25.62	29.07	24.81	29.11	24.96	28.57	25.07	28.56	24.90	28.60

*insufficient sample to analyze.

TABLE B-2. FINAL CORRECTED GAS VOLUMES

Run	Dry		Wet	
	ft^3	m^3	ft^3	m^3
Run I				
Stack	62.71	1.78	109.64	3.11
Combustion Zone	170.87	4.84	186.51	5.28
Run II				
Stack	64.68	1.83	95.30	2.70
Combustion Zone	172.57	4.89	183.57	5.20
Run III				
Stack	47.72	1.35	72.37	2.05
Combustion Zone	160.22	4.54	169.32	4.80
Run VI				
Stack	46.84	1.33	80.59	2.28
Combustion Zone	166.65	4.72	178.88	5.07
Run V				
Stack	46.76	1.32	76.91	2.18
Combustion Zone	131.41	3.72	146.39	4.15
Run VI				
Stack	82.99	2.35	122.71	3.48
Combustion Zone	172.52	4.89	195.27	5.53
Run VII				
Stack	45.75	1.30	76.94	2.18
Combustion Zone	140.63	3.98	160.18	4.54

TABLE B-3. LIQUID IMPINGER VOLUME DATA

Sample	Starting Volume Before Test (ml)	Volume After Test (ml)	Final Sample Volume (ml)	Volume of Water Collected (ml)
MA-I-SG-CI	200	1171	1171	971
MA-I-CG-CI	200	471	221	271
MA-I-CG-CI-A			250	
MA-II-SG-CI	200	826	826	626
MA-II-CG-CI	200	387	137	187
MA-II-CG-CI-A			250	
MA-III-SG-CI	200	702	702	502
MA-III-CG-CI	200	348	98	148
MA-III-CG-CI-A			250	
MA-IV-SG-CI	200	883	883	683
MA-IV-CG-CI	200	422	172	222
MA-IV-CG-CI-A			250	
MA-V-SG-CI	200	819	819	619
MA-V-CG-LI	500	730	500	230
MA-V-CG-LI-A			500	
MA-V-CG-CI	200	250	150	50
MA-V-CG-CI-A			100	
MA-VI-SG-CI	200	1019	1019	819
MA-VI-CG-LI	1200	1543	1293	343
MA-VI-CG-LI-A			250	
MA-VI-CG-CI	200	300	200	100
MA-VI-CG-CI-A			100	
MA-VII-SG-CI	200	834	834	634
MA-VII-CG-LI	1000	1293	1000	293
MA-VII-CG-LI-A			500	
MA-VII-CG-CI	200	290	190	90
MA-VII-CG-CI-A			100	

APPENDIX C

CALCULATION OF INCINERATOR PERFORMANCE

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APPENDIX C

CALCULATION OF INCINERATOR PERFORMANCE

The destruction efficiencies presented in Table 1-1 were calculated for each of the tests where the appropriate on-line and hot zone samples were taken. The data used in these calculations can be found in Tables 4-6, 5-2, 5-3, and 5-4.

The waste destruction efficiency (DE_{waste}) is based upon comparing the waste input rate to the waste emitted rate.

$$DE_{waste} = \frac{\text{waste input} - \text{waste emitted}}{\text{waste input}} \times 100\% \qquad \text{(C-1)}$$

Equation C-1 restated in another form, is

$$DE_{waste} = \frac{I_{waste} - [VFR_{gas}\ E_{waste}]}{I_{waste}} \times 100\% \qquad \text{(C-2)}$$

where:

I_{waste} = input rate of the waste = fuel feed rate x weight fraction of waste in fuel. Units are milligrams per second. Table 4-6.

VFR = volumetric flow rate of combustion gases from the burner. Approximately equal to input rate Table 4-6. Units are cubic meters per second.

E_{waste} = concentration of organic waste constituents in the combustion gas as determined by G. C. It is the sum of the waste constituents found in the probe wash, filter and sorbent trap samples from the combustion zone (Table 5-2). Units are milligrams per cubic meter.

Similarly the destruction efficiency for total organics ($DE_{total\ organics}$) compares the input rate of combined waste and auxiliary fuel to the emitted rate of all organic material found in the combustion zone samples.

$$DE_{total\ organic} = \frac{I_{fuel} - [VFR_{gas}\ E_{total\ organics}]}{I_{fuel}} \times 100\% \qquad \text{(C-3)}$$

where:

I_{fuel} = input rate of combined waste and fuel oil (when used). Units are milligrams per second. Table 4-6.

$E_{total\ organics}$ = sum of the concentrations of all organics found in the combustion zone samples. (Tables 5-2, 5-3, 5-4) Units are milligrams per cubic meter.

The waste destruction efficiency calculation for Test MA-V is presented below as an example. Initially I_{waste} is calculated, then VFR_{gas}, and finally E_{waste} is taken from 5-2, added to the equation to calculate DE_{waste}.

$$I_{waste} = 0.0341 \text{ kg/sec} \times \frac{1}{3} \times 10^6 \text{ mg/kg}$$
$$= 11{,}400 \text{ mg/sec}$$

where:

0.0341 kg/sec = total fuel feed rate Table 4-6

1/3 = C-5,6 weight fraction in fuel

Volumetric Flow Rate of Gas

$$VFR_{gas} = 0.568 \frac{\text{kg}}{\text{sec}} \times \frac{\text{mole}}{28.8\text{g}} \times 1000\text{g/kg} \times \frac{0.024 \text{ m}^3}{\text{mole}} \times \frac{294° \text{ K}}{273° \text{ K}}$$
$$= 0.51 \text{ m}^3\text{/sec}$$

where: $0.568 \frac{\text{kg}}{\text{sec}}$ = air feed rate Table 4-6

where: $0.568 \frac{\text{kg}}{\text{sec}}$ = air feed rate Table 4-6

$\frac{\text{mole air}}{28.8\text{g}}$ = estimated molecular weight of combustion gas

$0.024 \frac{\text{m}^3}{\text{mole}}$ = approximate molar volume of gas at 21°C

$\frac{294° \text{ K}}{273° \text{ K}}$ = volume correction based on temperature.

Waste Destruction Efficiency

$$DE_{waste} = \frac{11{,}400 - [0.51 \times <0.2]}{11{,}400} \times 100\% \qquad \text{(C-2)}$$

$$= >99.9991\%$$

The destruction efficiencies for total organics, $DE_{total\ organic}$ are calculated in a similar manner using equation C-3 and inputing the combined waste and auxiliary fuel feed and the concentration total organic found (Tables 5-2, 5-3 and 5-4).

APPENDIX D

ANALYTICAL CHEMISTRY DETAILS

APPENDIX D

ANALYTICAL CHEMISTRY DETAILS

The elements of this appendix consist of the interpretation of the instrumental data that led to the results discussed in Section 5. As part of the on-going effort to thoroughly characterize hardware and sample behavior in this relatively new analysis technology, extra effort was made to characterize certain control samples and monitor filter weights during their preparation. Details of this effort are also documented in this appendix.

D-1. Survey Analysis on Combustion Zone Filter Extracts

The material found in the solvent (methylene chloride) extracts of the combustion zone filters was surveyed for its qualitative nature by infrared spectrophotometry (IR) and low resolution mass spectrometry (LRMS). The IR data indicates that two main classes of compounds are present. The first is alkyl esters of phthalic acid. This commonly used placticiser and lubricant may have been in the waste feeds or may be a contaminant from the system. Whether one compound or several members of the family of these compounds is present cannot be determined from the IR scans alone. The second group of compounds is esters of fatty acids such as adipic and sebacic acids. The evidence for this is that the 2800 to 2900cm^{-1} IR region is more intense than that usually found on commonly occurring phthalate esters. Further evidence is shown by the LRMS data.

The LRMS data support these conclusions drawn from the IR data. The m/e 149 peak is quite evident, but is not the strongest peak in any of the mass spectra. For all phthalate esters in the available literature, this 149 peak, which is caused by the stable "anhydride plus 1 hydrogen" ion, is the strongest peak. Other m/e peaks in the sample such as 27, 29, 41, 43, 55, 57, 69, 71, etc., are stronger and this indicates that alkyl hydrocarbon groups, classically represented by this peak pattern, predominate. The presence of a peak at 167 atomic mass units (AMU) is indicative of di-n-octyl phthalate and dimthyl phthalate being present. A peak at 185 AMU is strong evidence for adipate and sebacate (fatty acid) esters.

It is important to note that the samples show no evidence of any of the hazardous constituents of the original waste feeds. That is to say, none of the constituents of the ethylene waste nor C-5,6 and its chlorinated homologues can be seen in the filter extract samples from their respective tests.

D-2. Survey Analysis of Control Sorbent Trap Extracts

This section presents the results of the analysis of solvent and sorbent traps that were examined as part of the analysis of the traps actually used in the sample trains during testing. This discussion is important from an analytical view point because significant amounts of background material were found in these control traps. As discussed later, the materials found in both the samples and controls are quite similar and the discussion here is a prelude to the discussion of the materials extracted from the test burn samples. Furthermore, results gathered here impact on the preparation and use of these traps in the future in order to lower their background contribution.

Two solid sorbent trap control samples were analyzed. The requirement for two samples resulted from the fact that two lots of pre-cleaned resin were used in the tests. The first control sample, MA-ST-C1, was extracted using a standard soxhlet extractor with pre-extracted thimbles into which the resin was placed after removal from the trap. The second control, MA-ST-C2, was extracted using the special apparatus which performs a Soxhlet-type extraction of the resin without its removal from the trap. The survey analysis results of these control samples show some weight differences depending on the extraction method used. The soxhlet extracted resin yields more weighable residue (Table D-1). The table also shows that the combined thimble and solvent blank also yielded a residue in spite of the prior extraction of the thimble, and the use of the highly pure solvents.

The first control trap, extract residue MA-ST-C1, contained esters of phthalic acid, perhaps an amide, and substituted benzene compounds. This material is present in spite of the extensive sorbent trap resin cleanup and pre-extraction of the Soxhlet thimbles and apparatus.

Table D-1. Extracted Material from Control Samples

Sample	Material Extracted by Pentane (mg)	Material Extracted by Methanol (mg)
MA-ST-C1 Control Sorbent Trap	1.370	12.350[1]
MA-ST-C2 Control Sorbent Trap	0.430	4.490
MA-ST-BLANK Soxhlet Thimble Solvent Blank	0.810	1.635

[1] The soxhlet thimble used for the C-1 control was not pre-extracted with methanol prior to extracting the sorbent resin with methanol. The reported value is believed to be higher than would have been achieved with a methanol pre-extracted thimble.

The infrared spectra of the, MA-ST-C1 residues were quite similar for both pentane and methanol extracts. The qualitative information is as follows:

Spectral Region	Assignment	Possible Compounds
3025	νC=C$^{/H}$	aromatic, possibly phthalates
3000-2800	νC-H	alkyl hydrocarbon
1740	νC=O	ester
1450	C-H bending	alkyl hydrocarbon
1680	νC=O	amide
1260	νC-N, δ-N-H or νC-O-C	ester or amide

The LRMS data from the MA-ST-C1 sample displayed the following pattern.

AMU	Assignment
27, 29, 41, 43, 55, 57, etc.	Alkyl hydrocarbon
77, 91, 105	Alkyl substituted benzene compounds such as toluene, ethyl benzene and xylene
149	Phthalate esters

The second control sorbent trap, sample MA-ST-C2, yielded considerably less residue than the first control resin. The reason is believed to be the elimination of the thimble as contributor of some of the contaminating materials, however the weight of residue obtained from resin itself also indicates a source of potential contaminants. The IR spectrum of the pentane extract residue was very weak and of little use. At the most favorable sensitivity, only the 3000 to 2800cm^{-1} region (alkyl hydrocarbons) was discernable. The methanol extract residue showed only traces of the methanol solvent and one peak at 1610 to 1520cm^{-1} (-NH$_2$ scissoring) which suggests, but which does not confirm an amine.

The material extracted from the second resin control sample by pentane had a LRMS peak pattern that was rather typical of the types of compounds seen in the C1 control sorbent trap and in many other sorbent trap extracts. Later discussion of other samples will refer to this pattern. The significant aspects of the low resolution mass spectra are as follows:

Mass Spectra Peak Pattern	Assignment
A dense peak pattern commonly called "pickets" containing stronger peak pairs at 27, 29, 41, 43, 55, 57, 69, 71, etc., increasing in 14 AMU increments (CH$_2$). These peaks usually extend up through the 111, 113 AMU peak pair befor they become no more intense than surrounding peaks.	Alkyl, normal and branched hydrocarbons either as a class of compounds or as substituents on other classes of compounds.

Mass Spectra Peak Pattern	Assignment
91, 105	Alkyl substituted benzene compounds, e.g., toluene, ethyl benzene styrene (benzoates are also possible).
111, 129, 185	Adipate, sebecate esters (fatty acid esters)
149	Phthalate esters
241	Di-butyl sebecate

The methanol extract of the MA-ST-C2 resin trap contained not only the same "picket" pattern, the substituted benzene pattern, and phthalate peaks described immediately above; but also contained a 279 AMU peak which, while not found in the TRW base of mass spectrometric data, has been identified as characteristic of dodecanoic (lauryl) sulfonates commonly found in detergents and surfactants.

D-3. Survey Analysis of Thimble and Solvent Blanks

The background sample characterization for sorbent traps was completed with an analysis of a third control sample obtained by extracting an empty thimble with pentane and methanol after it had already been pre-extracted with these solvents as per the standard resin extraction procedure. The amounts of recovered material are small in relation to the other samples but the LRMS data indicate the same basic types of compounds:

AMU	Assignment
Dense "pickets"	Alkyl hydrocarbons
149	Phthalates
111, 129, 185	Adipate, sebecate esters
167	Di-methyl phthalate
256, 73	Palmitic acid esters

There was insufficient sample in the extract aliquot to obtain a useful IR spectra.

D-4. Survey Analysis of Test Sorbent Trap Extracts.

This section presents the results of the survey analysis on the extracted material from the sorbent traps used in the sample trains. The procedures for the extracting these traps is discussed in Section 4.4, and the weight of extracted material is summarized in Table 5-4. In general, the composition of these materials from tests with the same waste are quite similar, and for ease of presentation the results are given in two groups: (1) MA-I, V, VI, VII, relating to the tests with C-5,6/fuel oil, and (2) MA-II, III, IV, relating to the tests with ethylene manufacturing waste.

MA-I, V, VI, VII

The IR spectra for pentane and methanol (and benzene in the three samples where it was used) extracts are very similar. However, there are some differences from which inferences can be made with respect to the overall composition. These differences are discussed below. The peaks found in the pentane extract residues and which are useful in determining the structure of these materials follow.

The pentane extracts of the solid sorbent traps yielded the IR spectra and assignments below. The methanol extract residues display the same pattern except that there is a trace of aromatic C-H absorption above 3000cm^{-1} and the carbonyl (C=O) peak in the 1750 cm^{-1} is somewhat stronger indicating that the methanol may be more effective in extracting the ester material. There is no evidence in the IR spectra that indicates the presence of any uncombusted C-5,6. The levels of sensitivity at which C-5,6 would be seen in this sample matrix were discussed in Section 4.4.2 and are on the order of less than 5 percent of the residue from each extract as shown in Table 5-4.

Spectral Region cm^{-1}	Assignment
2950	$\nu_{as}\ CH_3$
2920	$\nu_{as}\ CH_2$
2850	$\nu_s\ CH_3,\ CH_2$
1750 - 1730	$\nu_{C=O}$ ester
1700	$\nu_{C=O}$
1650 - 1500, weak	phenyl nucleus or weak amide
1460 - 1450	$\delta_{as}CH_3,\ CH_2$ scissoring
1380 - 1350, weak	$\delta_s\ CH_3$ bending of methyl group from alkyls, esters
1300 - 1250	asym C-O-C stretch; esters, ethers
1100 - 1050	sym C-O-C stretch; esters, ethers

The LRMS data of the sorbent trap pentane extracts confirm the general features of the IR spectra. The typical hydrocarbon fragment "picket" pattern is evident in all samples. Alkyl substituted benzene compounds are indicated (77, 78, 79, 91, 105, 133 AMU). Phthalate esters are also present but not as the predominant class of compounds. The presence of esters of fatty acids (adipic, sebacic) are shown by the 111, 129, 185 peaks in several of these samples.

The methanol extracts of the sorbent traps contained the same compounds. The 149 AMU phthalate peak was stronger in these extracts. A 45, 60, 74 AMU pattern was indicative of alkyl, monocarboxylic acids. Some of the fatty acid compounds produce these peaks. As a matter of routine examination of all LRMS data from all samples, mass spectral evidence of hexachlorocyclopentadiene (C-5,6) and any other cholorinated hydrocarbons were specifically and carefully searched for. None were detected. The sensitivity of the mass spectrometer solids probe analysis technique for searching for particular compounds in a sample is discussed in Section 4.4.2. The detectable level for a compound under the worst circumstance was 10 percent (w/w) of the sample residue being examined.

MA-II-, III, IV

The MA-II, III and IV sorbent trap extracts display differences in the compositional nature of the extracted material especially between that extracted by pentane and that extracted by methanol. The IR spectra for the pentane extract residues of MA-II, III, and IV are essentially the same as the pattern discussed earlier for MA-I-CG-ST. The MA-III spectrum is weaker than the others, but the major peaks are apparent. The aromatic composition of the MA-II, III, IV pentane extracts is greater than that for the MA-I baseline run. This is consistent with the high aromatic content of the ethylene waste. The spectrum of the MA-II methanol extract residues show the strong alkyl and carbonyl patterns discussed above with respect to the C-5,6 tests, but the MA-III and IV spectra show extremely small amounts of absorption in these areas. The esters and hydrocarbons previously mentioned are present at very low levels in these two samples. The only peaks in these spectra valuable for identification purposes are caused by small amounts of residual methanol in the sample after evaporation.

The LRMS data confirms the observation that the esters, etc., are present in these samples at lower levels relative to the others sorbent trap extracts. The LRMS data from the sorbent trap pentane extracts for Runs II, III, and IV again show distinct similarity to each other and with the patterns earlier described for the sorbent trap control samples:

AMU	Assignment
hydrocarbon pickets 41, 43, 55, 57, etc.	alkyl hydrocarbons or hydrocarbon substituents on other compounds
73 (strong peak) 77, 78, 79, 91, 105	C-O-R esters, ethers, etc., substituted benzene compounds
133	phenyl compounds, substituted benzenes, benzoates, phthalates

AMU	Assignment
149	phthalates
167	dimethyl phthalate
185	adipate and sebacate esters
p+14 (-CH_2) pattern from ∿207, 221, etc., out to AMU 600 and higher	hydrocarbon oils and greases

The LRMS data from the methanol extract residues of the sorbent traps for Runs II, III, and IV show the same pattern discussed above, but the patterns are less intense and indicate that the esters and automatic compounds are likely present at lower levels. This trend agrees with the IR data discussed above. Different patterns are evident in the methanol extracts but examination of the literature provided a multitude of compounds which ionize into some of the fragments listed above but there is not a sufficiently good fit of the literature data with the sample spectra in other areas of the spectrum to arrive at even a tentative conclusion as to what types of compounds are presents. It is stressed however that this spectra bears little or no resemblance with that of the original waste.

AMU	Assignment
31	primary alcohols, esters, or ethers
32	
48	
64	
65	
80	
81	
82	
95	
110	
113	possible furyl or similar ring ethers

Mass Spectrometer Analysis of Sorbent Trap Resins By Direct Probe

Additional LRMS direct probe analysis of the sorbent trap resins from selected tests was carried out to 1) determine the nature of the material, if any, which might still be absorbed on the resin after solvent extraction, and (2) gather additional information as to the source of the fatty acid esters and phthalic acid esters which are found in many of the samples.

Four samples were selected for analysis:

MA-ST-C1	pre-cleaned, unused resin
MA-I-CG-ST	base-line test with No. 2 oil
MA-III-CG-ST	second test with ethylene waste
MA-V-CG-ST	first test with C-5,6 waste/fuel oil

Resin samples from MA-III and MA-V were selected because the amounts of materials extracted from the sorbent traps for these tests were significantly lower than the recoveries obtained from the other tests with the same waste, leading one to suspect that there might be unextracted material still on the resin. A portion of the resin was placed in the solids probe of the mass spectrometer. The probe block was heated from 50° to 350°C at 100°C increments and the thermally desorbed constituents were then analyzed. This analysis provides no quantitative estimate of what might be present on the resin, it only provides qualitative information.

The results of the mass spectra of desorbed materials are summarized as follows:

Sample	Observations
MA-ST-C1	Only residual benzene (the third and final extraction solvent) and the 149 AMU phthalate fragment were noted at all temperatures.
MA-I-CG-ST	Benzene is the only compound seen at lower temperatures. A pattern at 60 to 64 AMU is apparent at 150°C and 250°C probe temperatures. At higher temperatures after benzene is driven off, a 91,105 pattern of substitued benzene can be seen. Phthalate ester peak at 149 is seen.
MA-III-CG-ST	Alkyl substituted benzene compounds were detected along with benzene, fatty acid esters and phthalate esters.
MA-V-CG-ST	Benzene and alkyl substituted benzenes, fatty acid and phthalic acid esters, dimethyl phthalate. Chlorinated species were specifically looked for and none were found.

The results of the analysis on the extracted resins from selected runs show that no new classes of compounds were thermally desorbed from the resins which had not already been determined as part of the solvent extracted material. The fact that traces of phthalate esters were found on the MA-ST-Cl control resin is evidence which supports the belief that the resins retained these compounds in low levels in spite of the resin cleanup procedures which were performed prior to the test program. The presence of these materials does not reduce the effectiveness of searching for toxic species; their presence only makes the task more difficult.

D-5. Survey Analysis of Scrubber Water Sample Extracts

The LRMS data from the carefully evaporated residues of the scrubber water extracts for tests MA-I through MA-IV were quite similar. They displayed a pattern shown by a mixture of alkyl hydrocarbons. The m/e 27 and 29 peaks are strongly present. These peaks are caused by the C_2H_3 and C_2H_5 fragments, respectively. This two-peak pattern is repeated every 14 atomic mass units (AMUs), i.e., 41 and 43, 55 and 57 (propyl, butyl, etc.). The 14 AMUs correspond to the $-CH_2$ fragment which is added to the molecular weight with increasing carbon number in a homologous series. There is evidence of constituents with molecular weights greater than 350. This is not uncommon with hydrocarbon oils. A compound with a molecular weight around 350 would contain about 25 carbon atoms. Evidence of the minor presence of phthalates is provided by the characteristic m/e 149 peak. The presence of substituted benzene compounds such as toluene, xylene, ethyl benzene, etc., at trace levels is also indicated.

Three additional peaks are present and are not in the 14 AMU peak pattern discussed above. These peaks occur at 247, 303, and 340. The compound(s) causing these peaks could not be identified using the available literature. Substituted benzenes and naphthalenes at low levels are also indicated, but xylene and toluene are not among those present.

The LRMS data had weak spectral patterns since only very small amounts of extract residue were found in the city water control sample, the fresh caustic scrubber control sample and the spent scrubber waters from MA-V - MA-VI as very little sample residue available for transfer to the mass spectrometer sampling system. The only signal shown by these extracts is the hydrocarbon cracking pattern discussed above. The highest detectable molecular weights are 139/141 although it is believed that higher molecular weight materials are likely to be present at undetected levels.

The LRMS spectrum of the MA-VII scrubber water extract residue is quite similar to the MA-I through MA-IV spectra discussed above, except that the m/e 247, 303, 340 pattern is absent. There is no evidence of any C-5,6 in the residue. The estimated levels at which these materials are seen in the mass spectrometer have been discussed in Section 4.4 and apply here.

D-6. Survey of the Ground Clinker by LRMS Direct Probe.

The LRMS data for the ground clinker form the tests with C-5,6/fuel oil display the hydrocarbon pickets at m/e 27, 29, 41, 43, etc., up to 69,

71. Traces of benzene and/or toluene were noted. Peaks at 35 and 70 were observed that can be described to monotomic and diatomic chlorine. These material are expected as combustion products. Hexachlorocyclopentadiene (C-5,6) and other chlorinated compounds organics were specifically searched for, but no trace of any chlorinated compounds were detected in the unextracted clinker. In addition, the typical 149 AMU peak for phthalate esters was found in all of these C-5,6 clinker samples. This is significant because these clinker samples were not extracted or otherwise processed except for grinding, and the probability of contamination during grinding is very small indeed. Thus, the presence of phthalates in the clinker is strong evidence for the presence of these materials in C-5,6 waste/fuel oil feed used in the tests. This can explain the presence of at least part, if not all, of these materials in the samples related to C-5,6 testing. Examination of the extracted clinker showed only traces of hydrocarbon pickets and methylene chloride, indication an extraction efficiency similar to that found for the ethylene test clinkers.

D-7. Weight Behavior of Combustion Filters During Analytical Preparation.

Weights were obtained on both the stack and combustion zone filters with their trapped particulate at several stages of their preparation as part of the on-going effort to understand the behavior of these samples during preparation and final analysis. They were first tared before their use and then weighed after the tests to determine the amount of particulate trapped. The weight of material extractable with solvent was then determined as well as the weight loss upon a low temperature plasma ashing. These weights are summarized in Table D-2. The data show that the amount removed by solvent extraction of the combustion zone filters ranges from 1 to 37 percent (13 percent average) of the total lost by solvent extraction and plasma ashing combined. Since the majority of the material removed by ashing is carbon in the form of soot, this result is not surprising. However, there are certain data which indicate that the solvent extraction process needs further study.

- Sample MA-II lost 66.3 percent of the original weight from plasma ashing and yet the visible nature of the filter does not indicate carbonaceous soot (Figure 5-1).

- All of the hot zone filters from tests I, II, III, and IV have consistently larger losses (relative to tests V, VI, and VIII) from ashing although the filters showed little or no visible soot. These losses may represent organic materials that are not being recovered by the solvent extraction. The amount of material lost by plasma ashing, averaged for all seven tests, represents 4 mg/m^3 of sample gas. This value would be the maximum amount of unextracted organics if more of the particulate were carbonaceous.

Table D-2. Filter Weights Through Analyses (mg)

Sample	Tare Weight Before Test	Weight After Test	Gain Due to Particulate	Loss on Solvent Extraction	Loss on Plasma Ashing	Remaining Weight on Filters	% Loss
Run I							
Stack	605.6	627.9	21.4	---	2.1	19.3	9.8
Combustion Zone	617.1	653.1	35.1	0.8	19.3	15.0	57.3
Run II							
Stack	609.9	641.6	30.8	---	13.7	17.1	44.5
Combustion Zone	606.6	709.7	102.2	0.6	67.2	34.4	66.3
Run III							
Stack	647.2	668.0	19.9	---	5.7	14.2	28.6
Combustion Zone	656.8	697.0	39.3	0.6	18.4	20.3	48.4
Run IV							
Stack	652.8	679.4	25.7	---	5.8	19.9	22.6
Combustion Zone	653.6	690.1	35.6	4.1	6.9	24.6	30.9
Run V							
Stack	643.8	681.9	37.2	---	0.6	36.6	1.6
Combustion Zone	655.7	684.0	27.4	1.5	9.9	16.0	30.7
Run VI							
Stack	658.8	752.7	93.0	---	-2.8[a]	95.8[a]	-3.0[a]
Combustion Zone	658.7	700.4	40.8	1.6	6.4	32.8	19.6
Run VII							
Stack	658.2	797.6	138.5	---	1.2	137.3	0.9
Combustion Zone	655.6	711.9	55.4	1.4	11.2	42.8	22.7

a - Weight Gain

D-8. Measurement of Particulate Loadings in the Combustion Zone vs Stack

Comparison of the measured particulate loadings, shown in Table D-3, between the combustion zone and stack values, also yields valuable information on the performance of the process and the ability of the sampling and analytical techniques to accurately measure that performance.

Table D-3. Particulate Mass Loadings

Run No.	Combustion Zone		Stack	
	mg/m^3	grains/std. ft^3	mg/m^3	grains/std. ft^3
I	7.3	0.0032	21.2	0.0092
II	20.9	0.0091	20.9	0.0091
III	8.7	0.0038	25.0	0.0109
IV	7.5	0.0033	20.4	0.0089
V	7.4	0.0032	36.2	0.0158
VI	8.4	0.0037	43.8	0.0192
VII	13.9	0.0060	113.5	0.0494

The fact that the concentration of particulate measured in the stack (downstream of a particulate scrubber) is higher than the level measured in the combustion zone is considered to be the result of a combination of four factors.

1. The stack was sampled superisokinetically. Rates at the stack ranged from 125 to 200 percent of isokinetic. At the hot zone, the rates were approximately 30 to 50 percent of isokinetic even though the hot zone train was operated at its maximum flow rate since it was not possible to put a nozzle on the hot zone probe. Superisokinetic sampling results in a bias toward a higher than actual small particulate/large particulate ratio. Sampling at lower than the isokinetic rate yields a bias in the opposite direction.

2. There was no nozzle on the hot zone probe. The use of a nozzle at Marquardt was ruled out as being impossible to protect and/or cool in the hot, corrosive combustion zone. It does appear possible, however, that the absence of a nozzle could also have resulted in substantially reduced collection of the large particulates at the combustion zone.

3. The combustion zone probe rinsings were not evaporated to dryness and weighed as were the stack probe rinses. The hot zone probe rinses were not evaporated because of the likelihood of losing or altering any organics which might be present. The significance of this factor can be estimated from the fact that the probe rinse weights from the stack were on the average equal to 30 percent of the filter particulate weight.

4. Salts generated by the HCl in the C-5,6 runs from the caustic in the scrubbing process were entrained in the scrubber mists and were carried to the stack filter, where they evaporated leaving a solid residue which was weighed as part of the particulate. A more efficient demister would likely reduce the salt emissions.

D-9. Inorganic Survey Analyses by ICPOES

To determine the inorganic composition of the particulate from the combustion and stack gases, selected filter acid digests and impinger solutions were first surveyed for 32 elements by ICPOES. These results are shown in Table D-4. Normally the ICPOES method is, in itself, highly accurate. However, solutions with high solids contents such as the samples from caustic impingers and acid digested filters, create interferences in the method which reduce its accuracy. Thus the ICPOES data does not agree with the AAS analyses as well as would generally be expected.

In addition to the elements shown in Table D-4, the following elements are determined by ICPOES but were not detected in the submitted samples: Au, As, Be, Eu, Pb, P, Se, Te, W, and U.

D-10. Wet Chemical Analyses for HCl, Cl_2, and CO_2

The caustic impinger solutions were analyzed for chloride, free chlorine, and carbonate to determine the amounts of each which were scrubbed from the combustion gases of the C-5, 6 tests. The results are listed in Table D-5. The large, 2-liter impinger (described in Section 4.3.2) was analyzed separately from the standard Greenburg-Smith impingers to determine the relative scrubbing efficiencies for each specie. No free chlorine was found in the impingers from test V, thus a less than value representing the detection limit of the technique is reported.

Table D-4. Elemental Survey of Selected Samples (mg/m^3)

ELEMENT	RUN I			RUN IV			RUN VI		
	COMBUSTION ZONE		STACK	COMBUSTION ZONE		STACK	COMBUSTION ZONE		STACK
	IMPINGERS	FILTER	FILTER	IMPINGERS	FILTER	FILTER	IMPINGERS	FILTER	FILTER
Ag	ND	NGTB <0.001	NGTB <0.001	ND	NGTB <0.001	NGTB <0.001	0.010	NGTB <0.001	NGTB <0.001
Al	0.006	NGTB <0.004	NGTB <0.11	0.052	NGTB <0.005	NGTB <0.030	ND	NGTB <0.009	NGTB <0.094
Ba	ND	NGTB <0.004	NGTB <0.14	ND	NGTB <0.001	NGTB <0.035	ND	NGTB <0.001	NGTB <0.11
Ca	0.025	NGTB <0.032	NGTB <0.53	0.024	NGTB <0.028	NGTB <0.33	0.056	NGTB <0.048	NGTB <0.23
Cd	ND	<0.001	<0.002	ND	<0.001	0.002	0.0004	<0.001	0.001
Co	ND	ND	ND	ND	ND	ND	0.028	0.001	ND
Cr	ND	<0.001	0.001	ND	0.001	0.001	0.009	0.019	0.008
Cu	0.018	<0.001	< 0.001	0.019	0.001	0.001	0.099	0.003	0.003
Fe	0.007	0.001	0.002	0.039	0.021	0.011	0.016	0.38	0.24
K	1.6	ND	ND	1.5	ND	ND	a	ND	ND
Mg	0.006	NGTB <0.009	NGTB <0.14	0.008	NGTB <0.007	NGTB <0.085	0.009	NGTB <0.013	NGTB <0.071
Mn	ND	<0.001	<0.001	ND	0.001	0.001	ND	0.022	0.022
Mo	ND	ND	ND	ND	ND	ND	0.076	ND	ND
Na	ND	NGTB <0.22	NGTB <1.7	ND	NGTB <0.34	NGTB <1.5	a	NGTB <0.42	6.2
Ni	ND	NGTB <0.002	NGTB <0.002	ND	0.002	NGTB <0.007	0.002	0.055	0.056
Si	1.4	---	---	1.6	---	---	1.2	---	---
Sr	ND	NGTB <0.001	NGTB <0.007	0.0003	NGTB <0.001	NGTB <0.002	0.017	NGTB <0.001	NGTB <0.004
Ti	ND	<0.001	<0.001	0.004	ND	ND	ND	<0.001	<0.001
V	ND	ND	ND	0.0004	ND	ND	0.002	ND	ND
Zn	0.004	NGTB <0.002	NGTB <0.079	0.009	NGTB <0.003	NGTB <0.020	0.020	NGTB <0.005	NGTB <0.15

NGTB - Not greater than background   ND - Not detected

a = The caustic impinger solution had very high backgrounds of Na and K

Table D-5. Caustic Impinger Analyses

Sample	Chloride		Chlorine		Carbonate	
	g Cl	liters HCl	mg Cl	liters Cl_2	g CO_2	liters CO_2
Run V						
Large Impinger	66.900		<0.5			
G.-S.* Impingers	3.175		<0.5			
Total	70.075	47.74	<1	<0.003		
Run VI						
Large Impinger	130.075		18.5		6.635	
G.-S. Impingers	3.120		203.4		7.680	
Total	133.195	90.76	221.9	<0.076	14.315	7.82
Run VIII						
Large Impinger	151.800		471.0		22.950	
G.-S. Impingers	4.350		322.5		6.989	
Total	156.150	106.41	793.5	0.269	29.939	16.31

* Greenburg - Smith